THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVI JANUARY 1951 No. 1

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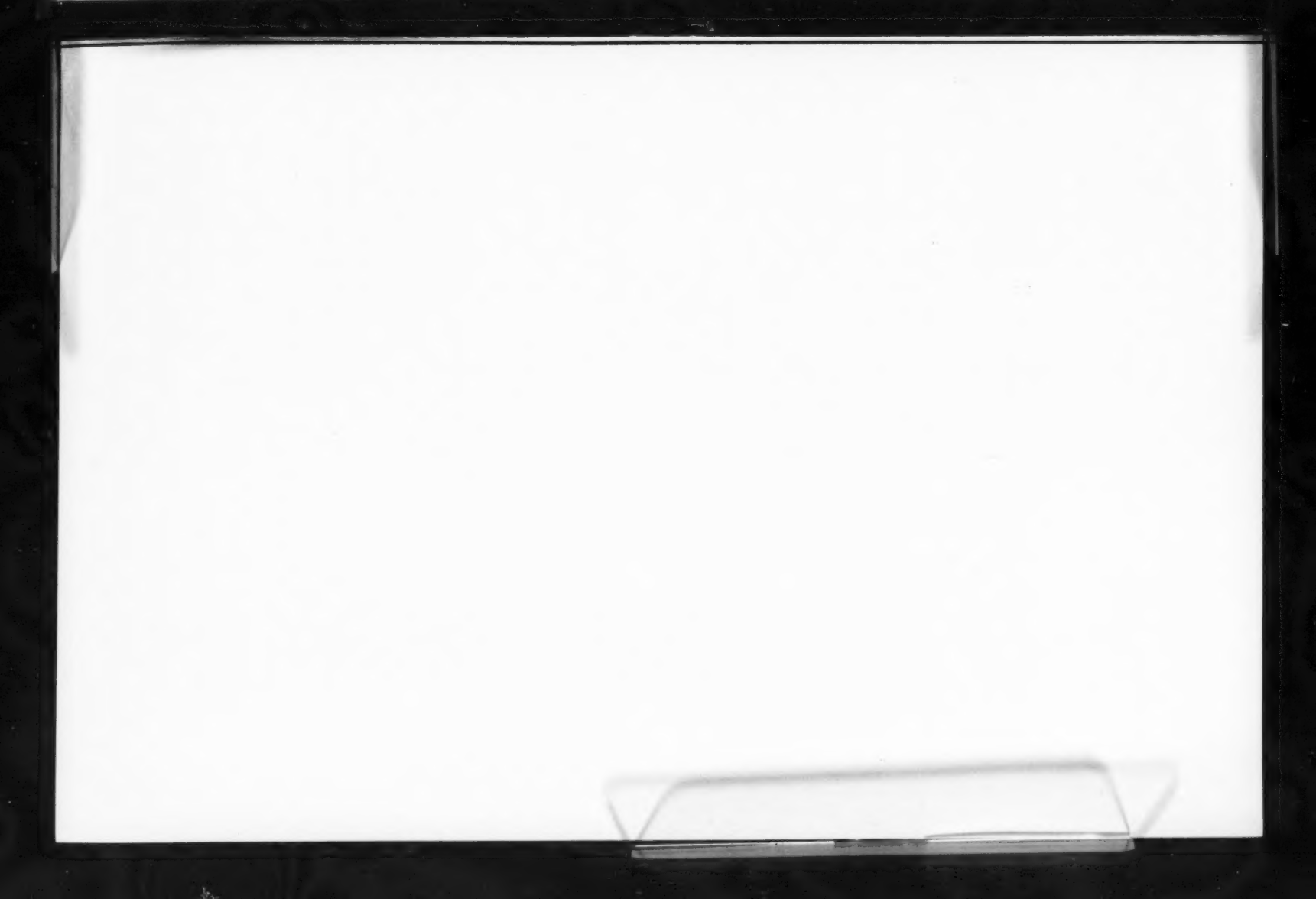

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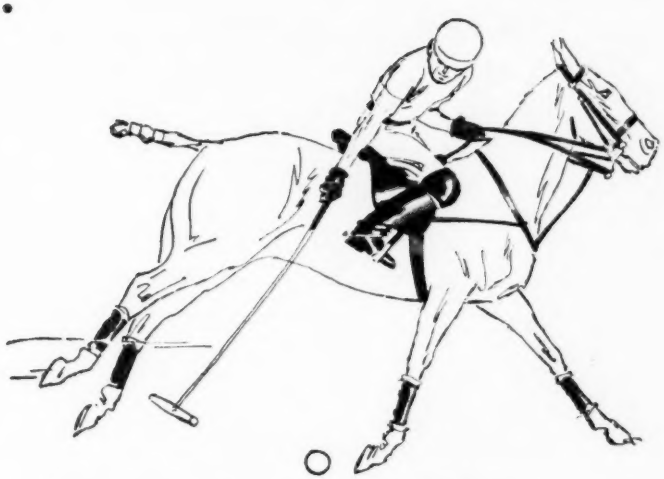

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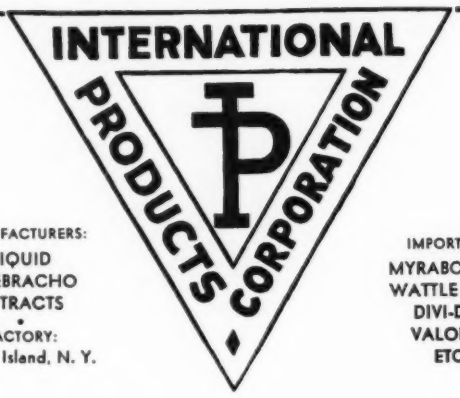

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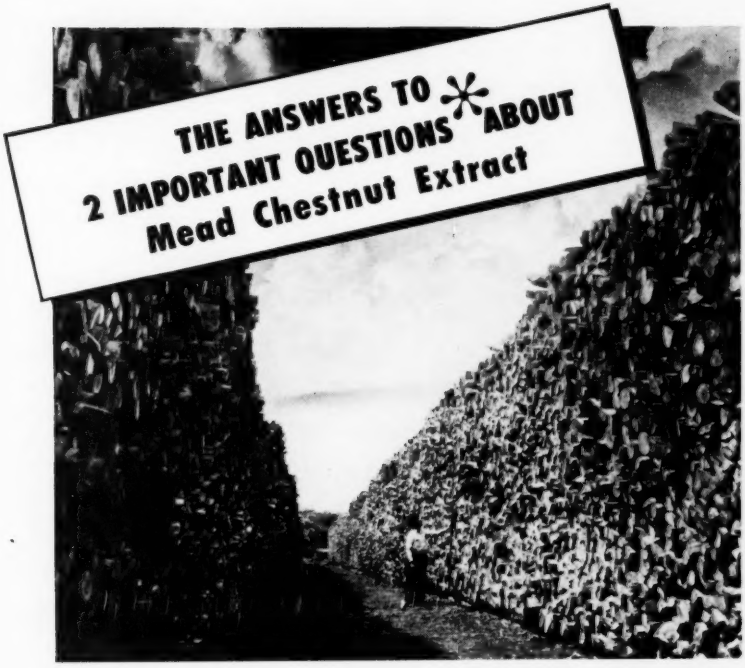

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B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

Ask about Mead Cold Soluble Chestnut Extract for retanned leathers. And—for more pounds of plumper leather—standardize on Mead Chestnut Extract.

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Vegetable Tannin	Tan Yard Yield (*white weight basis*)
Chestnut Wood Extract	67%
Tanning Material A	61%
Tanning Material B	63%

Calculate your tanning material costs on a leather basis as well as on a tan unit basis. Mead Chestnut Extract, producing four to six pounds more leather, means positive savings.

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Mol. Wt. 78.1
M.P. . . . . 100°C

Light buff colored solid in flake form. Rapidly soluble in water; slightly soluble in alcohol; insoluble in ether. Also available in solid form.

ANALYSIS

Na_2S	60 to 62%
NaCl	1.5% Max.
Other Na Salts	2.0% Max.
Fe	8 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	35% Min.

SHIPPING CONTAINERS

Steel drums . . . . 90 and 350 lbs. net

SODIUM SULFHYDRATE—NaSH

(sodium hydrosulfide)

Mol. Wt. 56.1
M.P. . . . . 55°C

Light lemon colored solid in flake form. Completely and rapidly soluble in water, alcohol and ether.

ANALYSIS

NaSH	70 to 72%
Na_2S	2.5% Max.
NaCl	0.8% Max.
Na_2SO_3 and $NaHCO_3$	0.4% Max.
Fe	5 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	28 to 26%

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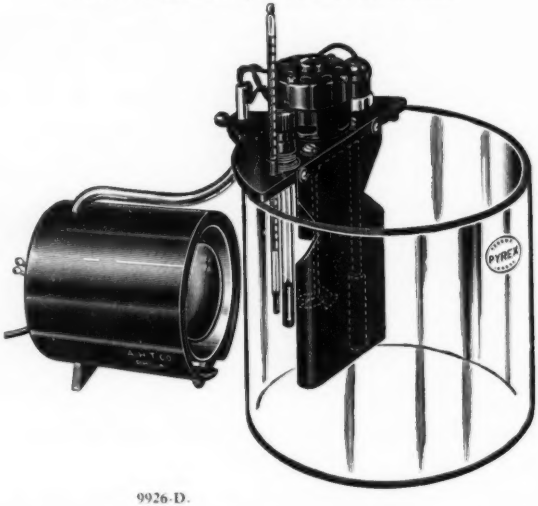

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VOL. XLVI JANUARY 1951 No. 1

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SECRETARY'S CORRESPONDENCE

Mr. H. B. Lincoln
L. H. Lincoln and Sons, Inc.
Coudersport, Pennsylvania

June 15, 1950

Dear Howard:

The officers of Council have instructed me to express to you their appreciation for your very fine service as chairman of the Ways and Means Committee.

Words seem inadequate to express such appreciation but be assured that your efforts, counsel, and advice have been a distinct service to the Association and more indirectly to the entire Tanning and Leather Industry.

Your many friends join in expressing these thoughts and hope that you, in wearing your A.L.C.A. key, may often reflect in the more pleasant aspects of the arduous responsibility of your chairmanship of the Ways and Means Committee.

I should like to add my personal thanks and appreciation for the privilege of working with you.

We all join in sending you our very best wishes.

Very sincerely yours,
Fred O'Flaherty,
Secretary.

FO'F:BJH

Dr. Fred O'Flaherty
Office of the Secretary
American Leather Chemists Association
Campus Station
Cincinnati 21, Ohio.

October 13, 1950.

Dear Fred:

Frankly I have had confidence in believing that my delay in acknowledging your most kind letter of appreciation on behalf of the A.L.C.A. Council would in no way be interpreted as a measurement of my appreciation.

Actually, I have had so little time for my attention to correspondence, I took it upon myself to feel I would still be in order, provided my expression of appreciation reached you in time for the Council Meeting.

Please believe me, no one could expect more kindly remarks than those you have included in behalf of Council. As a matter of fact, even in retrospect it is extremely difficult for me to appreciate the justification of such kind words. Being human, however, certainly I am going to accept them, remaining very proud of being in possession of such a letter.

In conveying this as my appreciation to Council,I only wish to add some simple philosophy of my own, namely most anything of a worthwhile

nature to an individual, either vocationally or invocationally should make it worthwhile for the individual to give as well as take. I believe this explains my personal pleasure and considered privilege if even a small portion of my past efforts have contributed even a little toward the continued success of the American Leather Chemists Association. I repeat my thanks to the Council and yourself.

Most sincerely,

HOWARD B. LINCOLN.

SECRETARY'S NOTICES

The National Bureau of Standards often receives inquiries from persons desiring the services of a laboratory or consultant for work on leather. In order to answer such inquiries, the Bureau is compiling a specialized list of organizations offering leather laboratory or consulting service to the public. Information questionnaires have been sent to all such organizations in Canada and the United States of which the Bureau has knowledge. However, if any readers of this Journal who offer such services have been inadvertently missed, they are invited to write to Mr. E. L. Wallace, Chief, Leather Section, National Bureau of Standards, Washington 25, D. C.

TO ALL MEMBERS:

Please refer to your copies of the Methods Booklet, if you find any corrections, changes in detail, or additions which should be made, please write me at once, as we are about to reprint the Methods Booklet. Please do this at once and address your remarks to me. Dr. Fred O'Flaherty, Secretary, American Leather Chemists Assoc., University of Cincinnati, Cincinnati 21, Ohio.

The Council of the A.L.C.A. will meet February 14, 1951 in New York City at the Hotel Statler (formerly Pennsylvania Hotel). All Committee Chairmen who desire to hold meetings in conjunction with Council are invited to notify the Secretary, so that proper meeting room reservations can be arranged for.

FRED. O'FLAHERTY, *Secretary.*

"We are seeking outstanding products including plastic and resinous finishes for leather, for wide distribution. Must be priced right for resale. Replies will be kept confidential." Send reply to–Box A. 1000, c/o Secretary, American Leather Chemists Assoc., University of Cincinnati, Cincinnati 21, Ohio.

The Physical Testing Committee has made the following recommendations:

The Committee recommends the following change in Conditioning Leather of Physical Tests E 3:

Samples shall be conditioned prior to testing in an atmosphere of 50 per cent ± 2 per cent relative humidity and at a temperature of 23°C. ± 1°C. until they have reached equilibrium, and shall be tested in that atmosphere. Samples shall be considered as having reached equilibrium when weighings made at hourly intervals show no progressive change in weight, and no change greater than ± 0.1 per cent. In general, at least 24 hours will be required to reach equilibrium.

If a conditioned room is available, samples may be conditioned in a desiccator or suitable chamber and removed therefrom one at a time and tested, provided: That the test is completed within 10 minutes and that the atmosphere in the room in which the test is made is not less than 45 nor more than 55 per cent relative humidity and not less than 21°C.

The required relative himidity in the desiccator or chamber may be maintained with a saturated solution of magnesium nitrate $Mg(NO_3)_2.6H_2O$ or a 52 per cent solution of sulfuric acid, the former being preferable.

That the — Method for Testing the Resistance of Leather to the Growth of Fungi be made an Official method.

That the Tearing Strength of Leather E 12 Method A, Tonque Tear be changed to read

"The jaws shall be not less than 1.25 inches wide."

This is considered as a change in detail only and with its approval by Council is adopted.

The Tannin Analysis Committee proposes the following Provisional Method for Copper Determination and it has been approved by Council:

Reagents Required:

Potassium Ethyl Xanthates—One gram of the salt is dissolved in 100 ml. of water. Solution to be made fresh at time of comparison.

Stock Solution of Copper Sulfate—3.9283 grams of $CuSO_4.5H_2O$ made to 1000 ml. One ml. is equivalent to 0.001 grams of Copper.

Standard Copper Sulfate Solution—Ten ml. of the stock solution are diluted to 1000 ml. in a volumetric flask. One ml. is equivalent to 0.00001 grams of Copper.

Procedure:

The ash is determined on a ten gram sample as described in the Procedure for Determination of Iron in Tanning Extracts. There are then two alternatives for the copper determination.

Alternative No. 1—Take up the ash with HCL, boil for five minutes, almost neutralize with ammonium hydroxide, and filter off the insolubles, collecting

the filtrate in a 200 ml. volumetric flask making it up to volume after cooling to 20°C. (The solution should be neutral or very slightly acid.)

Alternative No. 2—The filtrate from the ammonia precipitation of the iron and aluminum in the determination of Iron in Tanning Extracts may be neutralized and made to 200 ml. and the copper determined by comparison method as given below. (The filtration is made through some other material than filter paper, e. g., asbestos, as the copper combines with the cellulose in the filter paper.)

Comparison:

Place a 5 ml. aliquot in a 50 ml. Nessler Tube, add 10 ml. of Potassium Ethyl Xanthate solution (made fresh), make to volume and mix thoroughly.

To prepare standards—Make a series of standards containing 2 - 8 ml. of standard copper solution (1 ml equivalent to 0.00001 grams Cu.) in 1 ml. steps from a burette. Add 10 ml. of Potassium Ethyl Xanthate make to volume and compare with unknown after mixing thoroughly. Comparison to be made under a source of daylight from the North, holding the tubes in a vertical position two inches above a white sheet of paper. If the reading obtained is in the higher brackets 8 ml. of standards or over, repeat comparison using a 2 ml. aliquot of the sample.

Calculation:

5 ml. aliquot—

$$\frac{\text{ml. std. x 40 x 0.00001 x 100}}{\text{grams of Original Sample}} = \text{Per Cent Cu (As Rec'd Basis)}$$

2 ml. aliquot—

substitute 100 in equation in place of 40.

(1) It is advisable to use copper free water for all solutions and throughout the procedure.

(2) Aliquot containing 0.04 mg. iron interfere with the copper determination.

D. B. GAPUZ

It is with regret that the death of Dr. D. B. Gapuz is announced.

Dr. Gapuz was an official of the Bureau of Animal Industry in the Philippines. He came to the United States in 1942 under a Philippine Government grant and matriculated as a graduate student at the University of Cincinnati. With the advent of Pearl Harbor, he was compelled to delay his return to Manila until after the end of World War II. 1943 to 1947 Dr. Gapuz served as a staff member of the Tanners' Council Research Laboratory.

Dr. Gapuz was a graduate of the University of the Philippines and received his M. S. degree at the University of Cincinnati. Dr. Gapuz made many friends while in the United States, all who join in extending their sympathy to the wife and family.

DR. FRED O'FLAHERTY

W. R. ATKIN

The passing of Professor William Rearden Atkin on the 11th October, 1950 prematurely ended the brilliant career of a distinguished personality.

He was born on August 8th, 1890 at Heckmondwike and entered the Leeds University in 1908. After graduating with 1st Class Honours in pure chemistry and 1st Class Honours in the chemistry of leather manufacture, he was appointed research assistant to the late Professor H. R. Procter and commenced work in 1912 on the swelling of gelatin, which eventually led to the Procter – Wilson Theory.

He became Assistant Lecturer in the Leather Industries Department in 1913 – the year when Professor E. Stiasny succeeded Professor Procter and the late Mr. F. C. Thompson joined the staff as Demonstrator.

Professor Atkin always had a keen sense of duty. At the outbreak of the First World War, he was granted a commission and proceeded to France early in 1915. After being wounded at Ypres and again in the Battle of the Somme, Captain Atkin served as an Area Gas Officer until 1919 when he returned to the Leeds University as Lecturer in the Leather Industries' Department under Professor D. McCandlish. Until Mr. F. C. Thompson's tragic death in 1937 students had the wonderful experience of being trained by these three great personalities. Professor McCandlish and Mr. Atkin carried on this great work until the former retired last year and Mr. Atkin was appointed to the chair. He had high hopes and intended to extend the traditions of the Department but unfortunately his health began to fail.

It is impossible to give an adequate appreciation of Professor Atkin. He was a man of many parts. His ability as a scientist was outstanding and he was much sought after by his colleagues in the other Departments of the University. He was a brilliant lecturer and his clear elucidations of the most complicated topics will always be remembered by those who had the privilege of listening to him. He published about fifty papers on diverse subjects and each one is a contribution of our knowledge. He was an authority on the chemistry of gelatin and collagen, hide powder, the calculation of pH values, the acidity of tan liquors, chrome liquors and the deterioration and protection of leather.

But he was much more than a great scholar. His unfailing cheerfulness, his alert mind and his pungent wit made him a charming companion. He was always ready to extend a helping hand and many will feel a deep sense of personal loss. His activities were numerous. He took a prominent part in University life where he served on the Board of Science and Technology for many years and held office as Dean of the Faculty. He also acted as University Marshal with conspicuous success. A few years ago he gave the Leeds Philosophical Society's Christmas lecture to children. He was a Governor of the Heckmondwike Grammar School and a leading figure in the Air Training Corps.

His services to the International Society of Leather Trades' Chemists are equally outstanding. He was Hon. Associate Editor of the Journal from 1922 to 1923 and then Hon. Editor from 1924 to 1930. He served on many committees for about 35 years and was elected President for 1937 – 39. Owing to the outbreak of the Second World War he was Acting - President on behalf of Dr. Chambard until 1947.

So ends his crowded hour of glorious life but he will always be remembered by those who knew him, in the words of Professor McCandlish, as a soldier, scholar and friend.

DONALD BURTON.

Wet Tension Testing Studies as Influenced by Chemical Modifications of Collagen*

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The "bridging" theory of tannage has developed during the past twenty years chiefly as a means of explaining the effect of tannage on the shrinkage temperature and swelling of collagen. Gustavson [7] has reviewed the development of this concept. Its development as an explanation of the mechanism of tannage has paralleled the development of the theory that bridges between molecular segments play a significant role in establishing the properties of high polymeric systems. Indeed one of the earliest statements of a bridging theory of tannage was included in Meyer and Mark's monograph [18] on high polymeric organic natural substances.

The cross-bridging theory in polymer chemistry has received its chief support from studies of the vulcanization of rubber. Alfrey [1] has concluded "that the evidence supporting the presence of primary cross-links in vulcanized rubber, although indirect, is conclusive enough to warrant the confident use of the hypothesis". However, he cites the contrary view of Midgley [19] "that the effects of vulcanization are due to increased intermolecular associative forces, rather than primary valence links, between polyisoprene chains". Alfrey concludes further that increased associative forces also play a role in determining the mechanical properties of vulcanized rubber. Comparing ebonite and slightly vulcanized rubber, he notes that ebonite has a higher brittle point and a higher high-temperature modulus. The higher brittle

*This paper is taken from a dissertation presented by Keith H. Jacobson to the Faculty of the Graduate School of Arts and Sciences of the University of Cincinnati in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1949.

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point is believed by Alfrey to be due to the intermolecular associative forces, while the higher high-temperature modulus is the result of the primary valence network.

Wool keratin represents a protein fiber in which the existence of disulfide cross-bridges is said to contribute to the mechanical properties of the fiber. Harris, Mizell and Fourt [9] have shown that chemical modification of wool involving reductive rupture of the disulfide bond produces a much more stretchy fiber of lower strength. However, the reduced wool can be re-bridged by forming a bis-thioether linkage so that it will again show the original stress-strain characteristics of the unmodified wool. Harris and Brown [10] conclude that "it appears that the deficiencies exhibited by the synthetic protein fibers when wet may be attributed to the lack of sufficient, effective cross-links".

The basic assumptions of the work on rubber and on keratin are that the cross-bridges contribute to mechanical properties of the polymer. Meyer [17] who made one of the early statements of the bridging theory of tannage [18] has stated that tanning converts collagen fibers into a form in which they swell less and display greater mechanical strength. He compares the phenomenon of tanning to rubber vulcanization, attributing both to cross-linking. While it has been generally assumed that tannage contributes to the structural stability of collagen due to cross-bridging, Highberger [11] in reviewing the relationship of the structural stability of collagen and the mechanism of tannage has questioned this general assumption.

He presents data which show that vegetable, formaldehyde and *p*-benzoquinone tannages lower the dry tensile strength of small collagenous fiber aggregates. Compton [2] has confirmed this for formaldehyde tannage, and also found a lowered dry fiber strength for chrome tannage. Highberger [11] further notes that practical tanners agree that tannage decreases the tensile strength of hides and skins; he therefore insists that the increased shrinkage temperature due to tannage must not be attributed a priori to cross-bridging. Highberger also emphasizes that mechanical stability, hydrothermal stability and chemical stability can not necessarily be assumed synonomous.

Stubbings and Theis [28] have stated that "a tanning process which brings about cross-linking between adjacent polypeptide chains should cause an increase in wet strength. It is this distinction between wet and dry strength that should be investigated rather than a comparison between tanned and untanned dry strength alone." Harris [8] furthermore has emphasized that wet tension testing should be used to secure results which can be validly used in theoretical considerations. Harris' idea is that by working with a fiber swollen in water, the chains are separated to an extent so that van der Waals forces and probably also salt-bridge (electrostatic) forces are reduced so that tension testing can give an estimate of the role played by covalent bonds and hydrogen bonds.

This paper reports data on an initial investigation of the influence of tannage on the wet tensile strength of collagenous fiber bundles.

Experimental Methods

Wet Tension Testing Technique

Mono-directional fiber bundle aggregates of collagen were desired to minimize the influence of architectural factors. Highberger[11] and Compton[2] used small fiber bundle aggregates teased from kangaroo tail tendons for this purpose. These tendons are sold as surgical suture material, and as obtained were unprocessed except for splitting and drying. Highberger[11] has noted that "they are composed of nearly pure collagen, and give a very sharp x-ray fiber pattern identical with that given by other collagenous tissues." Neuman[20] has shown that collagen from the kangaroo tail tendon has the same amino acid composition as purified animal skin collagen of the types described by Highberger[12] and Buechler (See Jacobs[13]). The kangaroo tail tendon collagen shows the long spacing in an electron microscope but generally has somewhat less lateral bonding between filaments than does skin collagen[22, 23] which is probably reflected in the more mono-directional or parallel fiber array which we desired. Hence, we decided to use kangaroo tail tendon fiber bundle aggregates for our work.

We used tendons from two commercial sources. Table I shows the characteristics of the tendons from these two sources. They were given a 24 hour extraction with 10 per cent NaCl to remove soluble proteins, and then washed free of salt before testing. The data of Table I indicate the purity and identity of these two sources of tendons. The strengths of these tendons are statistically identical; hence we were able to use tendons from both sources.

The degree of variation in the strength of these tendons led us to select a lot of 25 tendons on which to evaluate the effect of any particular variable. The tendons as received were cut to a length of 17.8 cm. (7 in.), weighed, and randomized so that each lot included the full range of fiber aggregate weights (from 0.025 to 0.100 gram). This gave a lot of fiber aggregates weighing about 1.8 g. and including a uniform distribution of diameters up to about 2 mm.

These randomized lots were soaked for 24 hours in 10 per cent NaCl, and then in successive changes of distilled water until salt-free. These washed fiber aggregates were slowly dried first at 100 per cent relative humidity for 24 hours, and then at 50 per cent R. H. while awaiting "leading". "Leading" consisted of applying a lead fishing sinker to each end of the tendon by working the sinker around the tendon by the use of a vise. This was required to permit the samples to be held in the flat jaws of the tester without slippage.

The leaded fiber aggregates were rewet for 24 hours and then given a 10 lb. wet hysteresis test. In this test the fiber aggregates were loaded (at a rate of 0.6 lb. per second) to 10 lb. in the incline plane tester, to be described later, and then unloaded. These fiber aggregates were then relaxed in water

TABLE I

Characteristics of the Kangaroo Tendons

	Type A*	Type E*
Nitrogen - Per Cent (Dry Basis)	17.3	17.5
Collagen - Per Cent N x 5.62	96.9	98.3
Collagen - Reference (13) - Per Cent	96.5	97.6
Globular Proteins - (13) - Per Cent	2.7	2.0
Elastin–Keratin - (13) - Per Cent	0.8	0.3
Chloroform Extract - Per Cent	0.3	0.17
Ash - Per Cent	0.12	0.04
Shrinkage Temperature - °C.	62	62
Strength of Fibers		
No. in Group 1	18	20
Mean Breaking Length-Group 1-Km	24.4	25.3
Standard Deviation–Group 1	3.1	2.9
No. in Group 2	20	
Mean Breaking Length–Group 2–Km	24.4	
Standard Deviation–Group 2	3.6	
Cumulative Strength of Fibers		
No. of Fibers	58	
Mean Breaking Length - Km	24.7	
Standard Deviation	3.2	

*Type A—Secured from Armour Laboratories.
Type E—Secured from Ethicon Suture Division of Johnson and Johnson.

for 24 hours before being again tested, this time to a load sufficient to rupture the fiber aggregates. This hysteresis test was demonstrated to be capable of being repeated with identical results many times on the same fiber aggregate, and in all cases there was a very small but real hysteresis area between the loading and unloading curves.

An inclined plane instrument (Scott IP-4 Serigraph) loaded the fiber aggregate at 1.5 lb. per second during the tension tests. The instrument records the stress-strain curves on a pen-and-chart recorder; the stretch on the fibers is shown directly on the chart, while the load on the fiber can be calculated for any point on the load curve from the known total load on the instrument carriage. Our instrument had a maximum capacity of 25 lb., securable in 5 lb. increments. Since we were testing wet fiber aggregates we modified the instrument jaws to include a telescoping trough through which a slow stream of water flowed over the fiber aggregates during the testing.

A majority of the tendons broke at the tester jaws; however, this did not seem to cause any assignable difference in breaking strength when compared to breaks between the jaws. Compton[2] found that "jaw breaks" could be included without statistical effect on the error of the determination.

The "Mean Breaking Length" technique[11, 12] was used as a means of correcting for differences in fiber size. The broken fiber aggregates were re-

laxed for a day in distilled water, and then cut away from the lead sinker. Their length was measured, and they were dehydrated through two changes of acetone for a total of eighteen hours, followed by a 4 hour vacuum drying at 75°C. The dried fiber aggregates were weighed to 0.1 mg. on an analytical balance. Air drying was substituted for acetone dehydration where the fiber aggregates had been treated with acetone-soluble materials. Mean Breaking Length is calculated from this formula:

$$Km = 4.54 \times 10^{-3} \frac{BL}{W}$$

Km = Mean Breaking Length in kilometers
B = Breaking Load in Pounds
L = Length of Fiber in centimeters
W = Weight in Grams of Fiber Length, L
4.54×10^{-3} = Units Conversion Constant

Collagen Fiber Modifications

Fiber tannages were performed with a chrome tanning salt, vegetable tannins, formaldehyde, and a sulfonyl chloride. Other fiber aggregates were also treated with 2,4-dinitrofluorobenzene, hexemethylene diisocyanate, mercuric acetate, and tetrahydroxy-triphenylmethane. The different properties of these several substances required different methods of treatment which must be given in some detail.

The tannages were carried out in two different systems. For one method, which we may designate as a rocker-type tannage, the tendons were strung on a frame which was rocked up and down in the tanning solution in a battery jar. The solution to wet stock ratio was kept to approximately 10 to 1 by adding sufficient hide powder along with the 1.8 g. of hide substance from the fibers. The drum-type tannages were carried out in long test tubes, rotated about their long axis. Here the addition of hide powder was not required.

Chrome tannage was accomplished by the use of Tanolin-R, a commercially available, sugar-reduced, one-third basic chrome sulfate tanning salt. The rocker-type chrome tannage used 25 g. dissolved in 400 ml. of water and added in four portions to 60 g. of hide powder and the 1.8 g. of fiber, both pre-wetted. The tannage time was 24 hours, with no neutralization, and then the fiber aggregates were tested as described. The drum-type chrome tannages were carried out on pickled fibers, employing a NaCl (5 per cent) – sulfuric acid (pH 2) pickle, and adding the chrome liquor in several feeds until the amount of chrome (as oxide) given was about one-third the weight of the fibers. The tannage was carried out for 24 hours, after which the chrome solution was neutralized to pH 3.6–3.8 with borax.

A rocker-type tannage with quebracho was carried out in a 0.1 *M* acetate buffer at pH 4.9 over a two day period, using approximately 100 per cent tannin on the hide substance basis. The wattle tannage was a drum tannage,

starting at pH 5.0 in a non tannin solution. Wattle extract dissolved in pH 5, 0.1 *M* acetate buffer was added progressively, and the tannage continued for 16 days, lowering the pH to 4 on the twelfth day. The vegetable tanned tendons were held in a 0.5 per cent tannin solutions in all of the pre-testing wet operations to minimize detannage. Further, they were not dried in acetone after testing for the same reason.

The formaldehyde tannage was a rocker-type tannage, carried out in a phosphate buffer at pH 8.0. The amount of formaldehyde used was one per cent on the hide substance basis. The tannage time was 24 hours.

Because of the recent emphasis on sulfonyl chloride tannage [23], we carried out a combined formaldehyde sulfonyl chloride tannage. The formaldehyde tannage was carried out together with the fibers to be tested for only the aldehyde tannage. The aldehyde tanned fibers for the sulfonyl chloride treatment were dehydrated through acetone passage and placed in benzene. The fibers were then transferred to a solution of 10 ml. of C_{16} paraffinic hydrocarbon disulfonyl chloride (furnished by duPont) in 40 ml. of benzene. Drumming for 5 hours in this solution, stoving of the impregnated fibers at 45°C. overnight, followed by several hours of soaking in a 2 per cent Na_2CO_3 solution and restoving completed the tannage. The fibers were washed until neutral and then leaded and tested.

It was desired to add a bulky group in the protein molecule. Sanger [24] has suggested the usefulness of 2,4–dinitrofluorobenzene (DNFB) as a protein reactant. A major advantage of this material is that the reaction with protein occurs at room temperature. The fluorine reacts with active hydrogens in the protein molecule (especially – NH_2 groups), releasing HF, which is neutralized by sodium bicarbonate, which is present in amount equivalent to the amount of HF expected to be released.

The DNFB was prepared by a procedure analogous to the preparation of 2,4–dinitrochlorobenzene [3], using fuming nitric acid in place of the concentrated nitric acid. The DNFB was fractionated by distillation in vacuo. Melting point 26–27°C. (uncorr.). Proof of the identity of the compound was made by a nitrogen analysis, (using glucose to reduce the nitro groups), and by preparation of a derivative (dinitrophenol) by refluxing with sodium carbonate. This derivative melted at 111–114°C.; the literature value for 2,4–dinitrophenol is 114°C.

Since the collagen used in this investigation was unlimed, it was of interest to see if DNFB would react with amide groups. Dinitrophenyl-asparagine was prepared, and nitrogen analysis confirmed that the amide group does react.

In the reaction of DNFB with collagen, 25 of the tendons (weighing approximately 1.8 g., air dry) were soaked in two liters of a solution of 10 g. of sodium bicarbonate. They were then placed in a cylinder containing 600 ml. of water, and 0.76 g. of sodium bicarbonate was added, followed by the

addition of a solution of 1.5 g. DNFB in 50 ml. of acetone. The reaction was allowed to proceed for three and one-half hours with gentle stirring. The reacted tendons were soaked in an aqueous acetone solution, then in water, and were then put in an atmosphere of 100 per cent relative humidity and room temperature.

Hexamethylene diisocyanate and mercuric acetate are commonly regarded as bridging agents for proteins. Certainly they do possess the bifuntionality which a bridging agent should possess. Speakman[27] has claimed that "the most effective cross-linking agent for animal fibers is mercuric acetate. Amino, guanido, carboxyl and possibly imino groups are involved in cross-linkage formation——". The German literature has generally credited diisocyanates as bridging agents also, although Noerr and Hees[21] do not believe that hexamethylene diisocyanate cross-links collagen.

Hexamethylene diisocyanate (duPont) was redistilled in vacuo prior to use. Twenty-five acetone-dehydrated tendons were placed in 600 ml. of ether, and 0.7 g. of the diisocyanate dissolved in ether was added. The reaction proceeded for five hours with gentle stirring. The reacted, fiber aggregates were passed through successive changes of acetone, aqueous acetone and water before being tested.

A 0.2 *M* mercuric acetate solution in a buffer medium of 0.1 *M* sodium acetate – 0.1 *M* acetic acid was reacted at room temperature with fiber aggregates previously soaked overnight in the acetate buffer. The 25 fiber aggregates weighing about 1.8 g. were treated with 300 ml. of the above mercuric acetate solution, added in six 50 ml. portions during a 7 hour reaction period. The fiber aggregates were then washed in several changes of the acetate buffer and finally leaded before being tested.

Tu and Lollar[29] have shown that 2,4,2′,4′ tetrahydroxy–triphenylmethane produces a very good laboratory tannage with shrinkage temperatures over 90°C. Fiber aggregates were repeatedly impregnated with this compound in a saturated methanol solution during a three day period. The impregnated fiber aggregates were then fixed in a NaCl solution followed by water before being tested.

Method of Analysis

Lipid analyses were performed on 5 g. samples in a Soxhlet extraction, using chloroform as the solvent. The extracted fibers were ashed at 600°C. in an electric muffle. Nitrogen analyses were made by the Kjeldahl method with a copper catalyst and boric acid to receive the distilled ammonia. Chromium determination involved a micro method using perchloric acid for oxidation and sodium thiosulfate as the titrant. All analsyes were corrected for moisture determined by drying in vacuo at 75° C. for 18 hours.

Shrinkage temperatures were secured on a Theis Shrinkage Meter which had been modified to hold tendons. Water was the shrinkage medium.

Standard methods were employed to secure the statistical evidence described later. Davies [4] and Snedecor [26] adequately describe these methods.

Experimental Results

Table II summarizes the data secured by the methods just outlined. The column headed standard deviation gives a statistical expression of the variability of the data calculated from the relations: $s = \left[\frac{(x-x)^2}{n-1}\right]^{1/2}$. The hide substance data are calculated from per cent nitrogen times 5.62, and by difference from 100 they represent an estimate of the amount of uptake secured. However, for dinitrofluorobenzene and hexamethylene diisocyanate this estimate may well be erroneous.

Table III represents a statistical analysis of the data of the first three columns of Table II. Bartlett's test [4] for homogeneity of variance was applied to the variances of the twelve sets [variance (s^2) is the square of the standard deviation (s)]. The results showed some source of non-uniformity of variance. Examination of the data showed that this non-uniformity occurs in the data with wattle, with two divergent groups of results being represented. Bartlett's test shows the remaining eleven sets to possess uniform variance. With this background, the analysis of variance technique [4, 26] was applied to all the data, as well as the data excluding the wattle results. These calculations are summarized at the top of Table III. The results indicate that there are quite significant differences between the twelve groups of treatments and that except for the wattle results these differences are due to differences in the mean values, not the variances.

TABLE II

Summary of Data on Treated Fibers

Fiber Treatment	Mean Breaking Length Km	Number of Samples	Standard Deviation of M.B.L. "s"	Hide Substance Per Cent Dry Basis	Shrinkage Temperature °C.
Original Fibers–Cumulative Data	24.7	58	3.16	98.5	62
Chrome A (Rocker)*	19.8	22	2.58	93.6	84
Chrome B (Drum)*	28.9	13	3.84	86.3	100
Chrome C (Drum)*	22.0	21	4.16	81.5	100
Quebracho (Rocker)	19.6	22	3.30	90.7	70
Wattle (Drum)	23.7	11	6.86	77.0	73
Formaldehyde (Rocker)	12.2	25	2.76	95.2	80
HCHO–Polysulfonyl Chloride	14.8	21	3.13	95.6	77
Tetrahydroxy Triphenyl Methane	33.0	5	4.47	91.4	72
Dinitrofluorobenzene	22.8	18	2.46	97.0	62
Hexamethylene Diisocyanate	23.2	18	4.08	97.0	62
Mercuric Acetate	26.9	15	3.12	91.6	73

*Lot Chrome A — 1.8 Per Cent Cr_2O_3
Lot Chrome B — 4.5 Per Cent Cr_2O_3
Lot Chrome C — 7.6 Per Cent Cr_2O_3

TABLE III

Statistical Analysis of Mean Breaking Length Data from Table II

A. Analysis of Variance

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F-Test of Significance
	All groups of treatments			
Between treatments	5817.47	11	528.9	F = 528.9/
Within treatments	2914.48	237	12.3	12.3 = 43.0
Total	8731.95	248	——	Very significant
	Excluding wattle tannage			
Between treatments	5773.97	10	577.4	F = 577.4/
Within treatments	2443.53	227	10.75	10.75=53.7
Total	8217.50	237	——	Very significant

B. Comparison of Treated Samples to Untreated Samples

Treatment of Fibers	F-Test		t-Test	
	Calculated	Tabular 0.05 Value	t Calculated	Probability Per Cent
Chrome A (Rocker)	1.49	1.92	6.49	<0.1
Chrome B (Drum)	1.48	1.92	4.16	<0.1
Chrome C (Drum)	1.74	1.75	3.07	<0.5
Quebracho (Rocker)	1.09	1.74	6.36	<0.1
Wattle (Drum)	4.72	1.99	0.77	45
Formaldehyde (Rocker)	1.31	1.85	17.12	<0.1
HCHO–Polysulfonyl chloride	1.02	1.95	12.32	<0.1
Tetrahydroxy Triphenyl Methane	2.01	2.52	5.46	<0.1
Dinitroflurobenzene	1.65	2.07	2.35	<2.5
Hexamethylene Diisocyanate	1.68	1.81	1.64	<10
Mercuric Acetate	1.02	2.23	2.41	<2.5

In order to find the probable source of these differences we applied the variance ratio (F) test and Student's (t) test [4, 26] to the data to secure the results at the bottom of Table III. We compared each fiber treatment to the untreated fiber data; this is a logical binary comparison because it evaluates the effect of the treatments. It will be noted that the variance ratio is less than the tabular 0.05 value in all cases except the wattle tannage. Since there is no reason why the original variance had to be either less than or greater than the experimental variance, the tabular 0.05 value becomes the 0.10 probability level. Thus, the variances after treatment are not significantly different from that before treatment unless a 1 in 10 error has occurred. This applies to all except the wattle, which variance is significantly greater than the original variance, thus confirming our analysis of the results from Bartlett's test.

The results of Student's t-test shows that all but two of the changes in the mean are significant. The probability shown is the probability that differences

as great as those secured could be due to pure chance. Hence, we may conclude all of the treatments except the wattle tannage and the treatment with hexamethylene diisocyanate have significantly changed the mean breaking length, unless a 1 in 40 or worse error has occurred.

Discussion of the Results

It is noted that the treatments have produced significant increases as well as decreases in the mean breaking length of the collagen fibers. Further, the wet strength of the fibers does not correlate (correction coefficient is only -0.02) with the shrinkage temperature. This reemphasizes the conclusion of Highberger[11] that mechanical stability and hydrothermal stability cannot necessarily be assumed to be synonymous.

The increased mean breaking lengths with 2,4,2′,4′-tetrahydroxy triphenyl methane, chrome B, and mercuric acetate are particularly interesting. Most of the fiber aggregates treated with tetrahydroxy triphenyl methane were too strong to be broken on our inclined plane instrument. It is logical to assume that the fiber aggregates which did not break were even stronger than the five that did break and hence that the true mean breaking length with this tannage is not less than the recorded value of 33. The amount of uptake of tetrahydroxy triphenyl methane is low, and the shrinkage temperature is 20°C. lower than Tu and Lollar[29] observed on pieces of calfskin tanned with this same material. The increased mean breaking length with Chrome B is in contrast to Chrome C, which is tanned with more chrome secured from a similar drum tannage, as well as the results with the rocker chrome tannage. Mercuric acetate is considered a protein bridging agent, and it is noted that the wet strength of the fibers has been increased. Is it therefore logical to conclude that cross-bridging has been proven by this increase in the wet strength of the fiber aggregates from the three treatments?

An affirmative answer to the above question then raises the question of interpretation of the lack of change or the decrease of the wet strength from the other treatments. Flory, Rabjohn and Schaeffer[6] have recently found that vulcanization of rubber with bifunctional disazo-dicarboxylates leads first to an increase and then to a decrease in the tensile strength of the vulcanized rubber. Since the vulcanization is attributed to cross-bridging, it therefore must be concluded that cross-bridging does not necessarily increase the mechanical strength of the polymer. These decreased fiber aggregate strengths may not therefore necessarily be concluded to be inconsistent with the bridging hypothesis.

It may further be noted that Elod and Zahn[5] have found that butanediol-bis-chloromethyl-ether decreases the strength of wool fibers, even though stability of the fibers to chemical and thermal decomposition increased. They describe the reaction as one of cross-bridging. Here again we see a lack of correlation between mechanical and hydrothermal stability of a fibrous protein.

Another factor which may be significant is the observation of Mao and Roddy[16] that tannage of gross pieces of heel tendon collagen does not decrease the dry strength of small teased fiber bundles while tannage of the small teased fiber bundles does decrease the dry strength of these fiber bundles. This might be the resultant of the case-hardening effect from the tannage of small fiber bundles.

Nutting and Borasky[22] have described collagen as having all its substance crystalline with the orderliness of the spatial packing everywhere less than perfect. This would seem to indicate rather strong forces stabilizing the polypeptide array, probably in a fairly extended state. These forces would seem to be the electrostatic forces due to the charged side chains (the salt-bridge forces) and the hydrogen bonds between the peptide links as well as those between uncharged polar side chain groups, especially hydroxy. In native collagen, strong covalent forces are not probable. These forces stabilizing collagen are thus individually rather weak, and native collagen has its high wet strength because of its highly ordered polypeptide array which permits these weak forces to be effective because of their number. This is analogous to nylon which has high wet strength and low stretch because of its close packed hydrogen-bonded peptide links, but which is very weak if this orderly array is not present.

Short spacing x-ray studies and measurements of birefringence as a function of tannage[22] have been interpreted to indicate that tannage decreases the orderliness of the fibrous array of the collagen. The long spacing x-ray studies and electron diffraction studies have not shown as much influence of tannage, but Nutting and Borasky[22] note that formaldehyde tannage caused some changes in the characteristic long spacings, and that the fibrillation of chrome tanned cowhide was imperfect. These observations would emphasize the effect of tannage in disordering collagen and hence lessening the effectivity of the inter-peptide-chain forces.

The greatest increase in the strength of the collagen fibers which we found was only a quarter of the original strength of the fiber. Yet, rubber shows a many-fold increase in strength after vulcanization, which is assumed to be a cross-bridging phenomena. Hence, though the present data cannot be used to prove or disprove a bridging mechanism, it would seem that if bridging does occur, it has a minor influence in comparison to the influence of bridging in other macromolecules. This may be a reflection of the fact that the bridges in vulcanized rubber or keratin are covalent bridges, a very improbable bridge for most tannages. It may be emphasized that the effect of the tannage in disorganizing the fibrous array seems to play a larger part than bridging in establishing the mechanical properties of the tanned fibers.

It may also be noted that increased shrinkage temperature is not necessarily an indication of bridging. Meyer[17] describes the shrinkage temperature of collagen as a two-dimensional solution of the crystallites in the water of im-

bibition. Certainly, the shrinkage temperature phenomena involves both a temperature effect and a hydration effect. The dry shrinkage temperature of collagen would be more analogous to the polymer melting point, which is commonly considered an indication of bridging. Kremen and Lollar[14] have noted that chrome tannage of limed collagen does not change its dry shrinkage temperature. Further, Lungren[15] notes that isoelectric keratin shrinks in water at 45–47°C. Since keratin is supposedly stablized by disulfide bridges, while collagen is not, it seems inconsistent that isoelectric collagen, without covalent cross-bridges, should have to be heated to 62–64°C. in water to permit shrinkage. It therefore seems inconsistent to assume that bridging must occur when the wet shrinkage temperature is increased.

Summary

Data have been presented on the effect of tannage and other treatments of native collagen fiber aggregates (from the kangaroo tail tendon) on the wet strength and wet shrinkage temperature. There is no correlation between these two factors in the data presented.

The implications of these results to the bridging theory of tannage is discussed. Although the bridging theory is attractive, it is emphasized that more evidence is needed to prove or disprove it. Only an integrated study of the chemical, hydrothermal and mechanical properties of collagen as influenced by tannage can furnish valid evidence on this question; results from the use of several techniques are currently being secured and will be reported later.

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Stratigraphic Distribution of Sodium Chloride and Water in Fresh and Brined Steer Hide*

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Recent studies have demonstrated that the distribution of chromic oxide in leather (Kritzinger & Theis, 1948) and the distribution of basic and dicarboxylic acids in animal skin (Stubbings and Theis, 1949) show variability from one stratum or layer to the other. These results were obtained by sectioning the hide or leather parallel to the grain surface into ten or fifteen slices. Earlier stratigraphic studies had been based on the splitting of the hide or leather into three to six layers. Grease distribution in leather (Balderston, 1922), salt and moisture in hides (McLaughlin and Theis, 1922) and lipids in steer hides and in sheep skins (Koppenhoefer 1936, 1938) were investigated on this basis.

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The present paper reports the results of an investigation of the stratigraphic distribution of salt (NaCl) and water in fresh steer hides and in steer hide subjected to a variety of experimental brining conditions.

Methods

All samples of steer hide were taken from fresh steer hides in the bend area about half way between the shank and tail and about four to six inches from the edge. Each experiment was repeated three times using a different steer hide each time. The samples were fleshed and clipped to eliminate any variability due to adhering adipose tissue or long hair. The clipped and fleshed squares of steer hide after being subjected to the experimental conditions were sampled by cutting out six to eight squares, each measuring about a square inch. These squares were sectioned on the freezing microtome into ten slices, parallel to the grain, all of the slices from the same stratum of all of the pieces constituting a composite sample which was then analyzed for salt (NaCl) and moisture.

In order to subject the grain and flesh surfaces of the hide to different liquids, the piece of hide was clamped between flanges connected on either side with a two inch pipe which curved upwards so that it could hold the liquids in contact with the respective surfaces (Figure 5). These experiments were run in duplicate, the two discs of hide (2 inches in diameter) each being cut into quarters and sectioned prior to analysis. The average results were computed from three such pairs of experiments. The solutions on each side of the clamped hide were analyzed for salt, moisture and protein. The layerwise distribution of salt and water in hide pieces was determined under the following conditions: 1. In normal fresh steer hide; 2. In fleshed steer hide immersed in saturated brine for four hours, 24 hours and 4 days; 3. In fleshed steer hide after treating the flesh side with saturated brine and the grain side with distilled water for 24 hours and for 4 days; and 4. In fleshed steer hide after treating the grain side with saturated brine and the flesh side with distilled water for 24 hours and 4 days.

Results and Discussion

1. *Normal Fresh Hide*

The distribution of salt and moisture and the degree of saturation of the ten layers of fresh (untreated) steer hide are shown in Table I and Figure 1. The thickness of the hide varied from 3.6 mm. to 5.4 mm. so that each stratum represents from 0.36 mm. to 0.54 mm. of the hide. In general, the first three layers (1.05 mm. to 1.60 mm.) represent the region the hair follicles and the remaining seven layers represent the corium of the hide.

The results in Table I and Figure 1 show that moisture of a normal hide is highest in the region of the hair follicles and decreases towards the center of the hide. The salt content is slightly higher in the hair-follicle area and

TABLE I

Stratigraphic Distribution of Sodium Chloride and Water in Bend Area of Fresh Steer Hide (Av. of Three Hides)

Stratum	Water	Sodium Chloride	Saturation
	Per Cent		
1 Epidermis	70.2	0.80	4.17
2	73.6	0.76	3.90
3	70.8	0.74	3.90
4	66.4	0.71	3.90
5	63.8	0.65	3.79
6	63.4	0.72	4.17
7	63.5	0.69	4.05
8	64.3	0.69	4.43
9	65.8	0.75	4.05
10 Flesh Side	63.5	0.66	3.79
Average	66.5	0.71	4.02

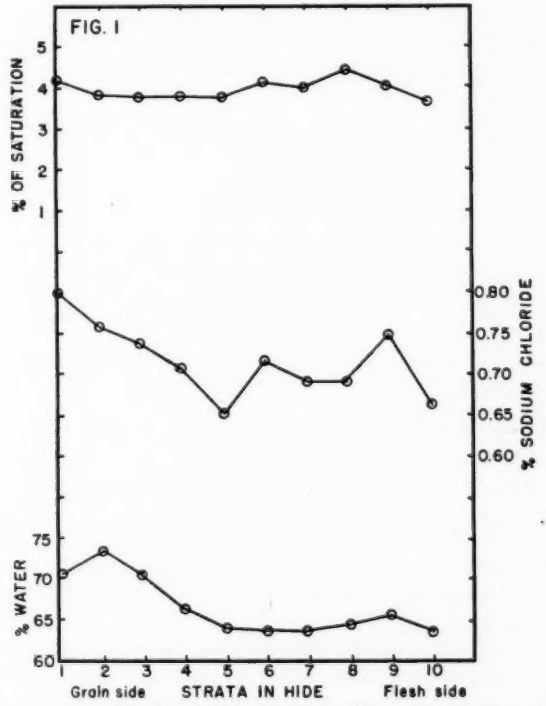

FIGURE 1.—Stratigraphic Distribution of Sodium Chloride and Water in Fresh Steer Hide (Average of Three Hides).

lower in the corium. However, the hide moisture is only about 4 per cent saturated with salt in almost all of the layers of the hide. These results are in general agreement with the findings of McLaughlin & Theis (1922).

2. *Hide brined 4 hours in saturated brine.*

The results of these experiments are shown in Table II and Figure 2 and demonstrate that the salt content has increased throughout the hide, ranging from 5 per cent in the hair-follicle area to 13 per cent on the flesh side. The moisture is still highest in the hair-follicle area and lowest in the lower part of the corium. The per cent of saturation shows a rising gradient from just below the epidermis to the flesh side.

TABLE II

Stratigraphic Distribution of Sodium Chloride and Water in Steer Hide Brined for 4 Hours in Saturated Brine (Av. of 3 Hides)

Stratum	Water	Sodium Chloride	Saturation
	Per Cent		
1 Epidermis	59.0	5.2	31.07
2	65.8	5.0	26.79
3	63.9	5.1	28.04
4	59.3	5.0	29.66
5	56.3	5.4	33.34
6	53.8	6.4	40.16
7	50.4	7.4	48.87
8	53.6	9.4	55.69
9	52.8	10.9	65.16
10 Flesh Side	56.4	13.3	73.30
Average	57.1	7.3	43.2

3. *Hide brined 24 hours in saturated brine.*

After being immersed in saturated brine for 24 hours, the moisture of the hide has decreased throughout the hide (Figure 3, Table III), the greatest reduction in moisture being in the hair-follicle region so that the moisture gradient is the reverse of that found in fresh hide. The salt content is lowest in the center of the hide. Due to the decrease in moisture and the increase in salt content, the hair-follicle region shows the highest per cent of saturation. This can be explained by the fact that the brine in contact with the epidermis is withdrawing moisture rapidly while the salt is entering from the flesh side and accumulating in the hide. On the basis of subsequent experiments it will be shown that from the epidermal surface salt enters the hide very slowly and in minute quantities.

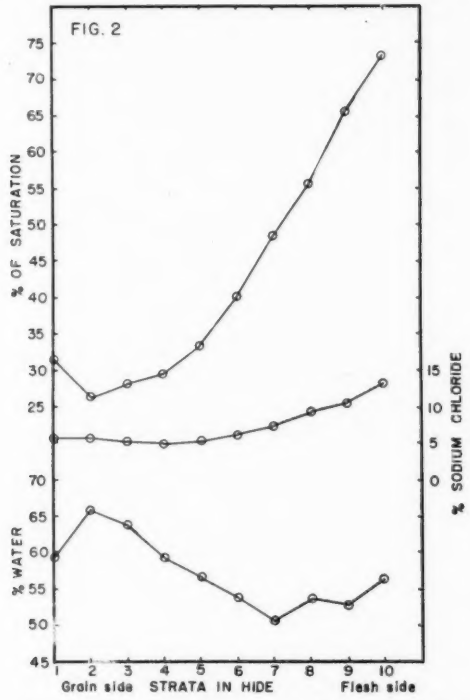

FIGURE 2.—Stratigraphic Distribution of Sodium Chloride and Water in Steer Hide Brined for 4 Hours in Saturated Brine (Average of Three Hides).

TABLE III

Stratigraphic Distribution of Sodium Chloride and Water in Steer Hide Brined for 24 Hours in Saturated Brine (Av. of Three Hides).

Stratum	Water	Sodium Chloride	Saturation
	Per Cent		
1 Epidermis	44.2	12.6	84.1
2	47.1	13.1	82.2
3	46.9	12.7	80.3
4	46.2	12.3	79.6
5	47.2	12.1	76.9
6	47.1	12.7	80.3
7	46.4	12.7	81.8
8	48.5	13.1	80.3
9	52.9	13.5	78.8
10 Flesh Side	56.5	14.3	75.0
Average	48.3	12.9	79.9

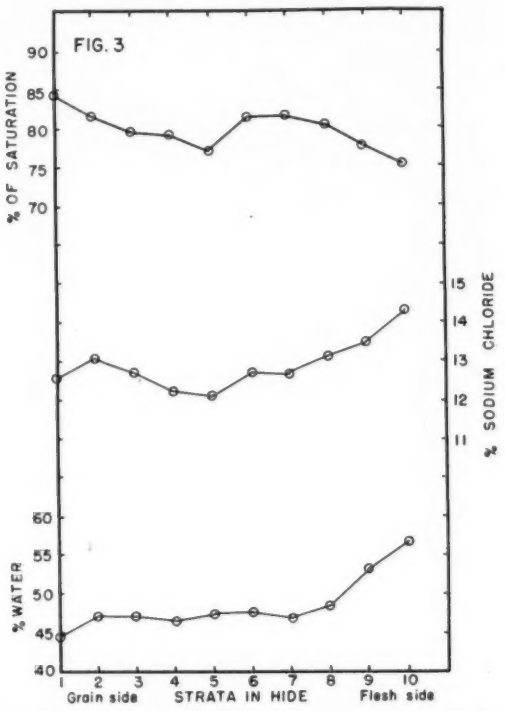

FIGURE 3.—Stratigraphic Distribution of Sodium Chloride and Water in Steer Hide Brined for 24 Hours in Saturated Brine (Average of Three Hides).

4. *Hide brined 4 days in saturated brine.*

The results of these experiments (Table IV and Figure 4) demonstrate that the salt content is lowest in the center of the hide while the moisture is only slightly lower in the center, resulting in this central region being the least saturated part of the hide. The increase in moisture after 4 days of brining as compared to 1 day of brining indicates that after two days of continuous brining the hide picks up moisture as well as salt. This is supported by experiments (not reported here) which measured the weight changes in brined hides following prolonged brining.

5. *Hide treated for 24 hours with saturated brine on flesh side and distilled water on grain side.*

The hide which had been clamped between flanges (Figure 5), during the experiment was sectioned and analyzed (Table V and Figure 6).

TABLE IV

Stratigraphic Distribution of Sodium Chloride and Water in Steer Hide Brined for Four Days in Saturated Brine (Av. of Three Hides).

Stratum	Water	Sodium Chloride	Saturation
	Per Cent		
1 Epidermis	51.2	16.1	85.13
2	51.1	16.3	91.57
3	49.7	15.5	89.79
4	48.9	14.9	88.27
5	49.4	14.4	85.89
6	50.2	14.5	84.99
7	50.6	14.5	84.49
8	52.8	15.8	87.25
9	53.1	16.4	89.90
10 Flesh Side	52.1	16.0	87.78
Average	50.9	15.4	87.51

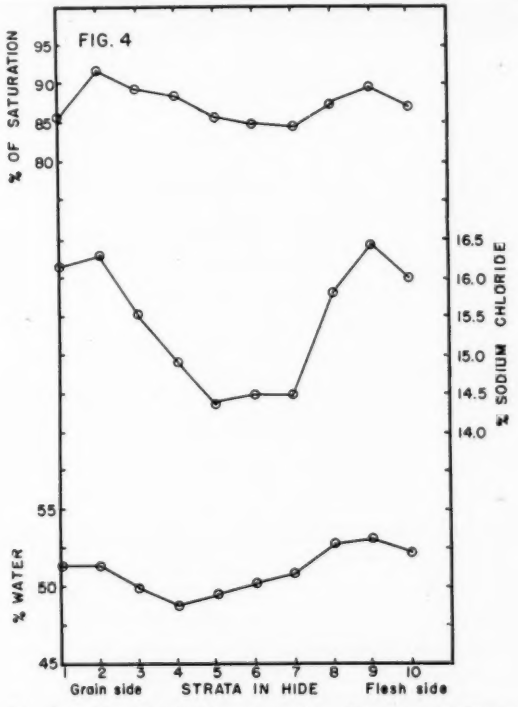

FIGURE 4.—Stratigraphic Distribution of Sodium Chloride and Water in Steer Hide Brined in Saturated Brine for 4 Days (Average of Three Hides).

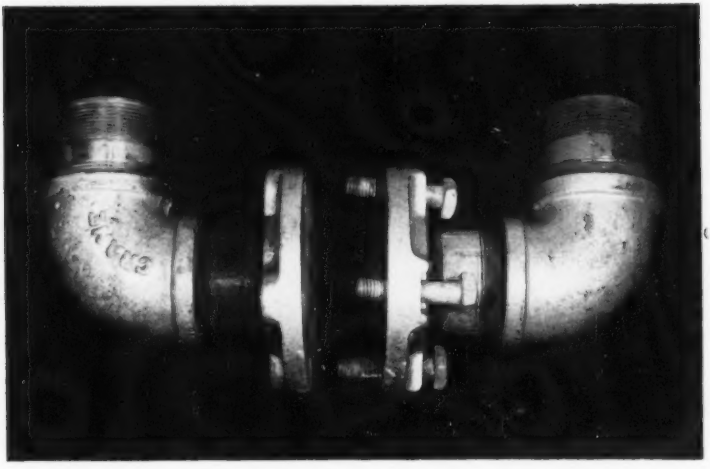

FIGURE 5.—Apparatus used to clamp hide pieces between flanges thus making it possible to subject the grain and flesh surfaces to different liquids.

TABLE V

Stratigraphic Distribution of Sodium Chloride and Water in Steer Hide Treated for 24 Hours with Saturated Brine on the Flesh Side and Distilled Water on the Grain Side (Av. of Three Hides).

Stratum	Water	Sodium Chloride	Saturation
	Per Cent		
1 Epidermis	61.9	12.7	64.52
2	63.7	15.0	72.48
3	61.5	14.7	72.85
4	56.2	13.4	72.85
5	53.1	12.7	73.01
6	51.8	12.3	73.85
7	51.6	12.5	73.76
8	51.7	13.0	76.06
9	53.2	12.9	73.76
10 Flesh Side	53.2	13.2	75.39
Average	55.8	13.2	72.75

The moisture was highest in the hair-follicle area and lowest in the corium. The salt content was always highest in the layer just below the epidermis and lowest in the epidermis itself and in the corium. Thus the epidermis is less saturated with salt, while the other layers are uniformly saturated. The higher salt content just below the epidermis is interesting in view of the fact

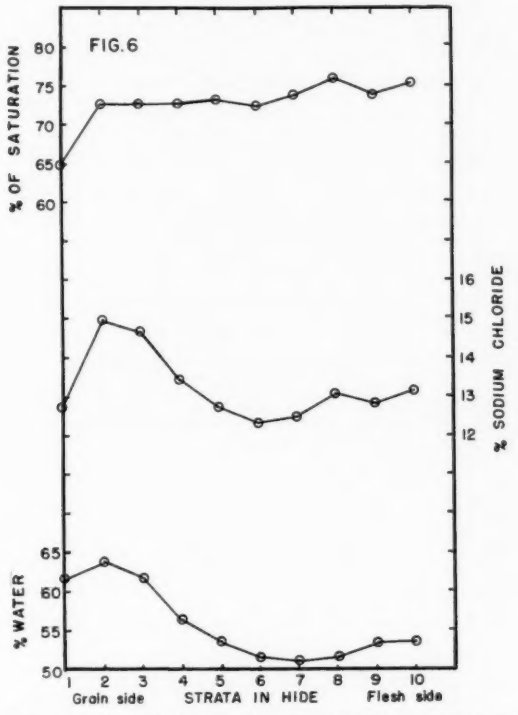

FIGURE 6.—Stratigraphic Distribution of Sodium Chloride and Water in Steer Hi Treated for 24 Hours with Saturated Brine on the Flesh Side and Distilled Water on the Grain Side (Average of 3 Hides).

that the salt supply is on the flesh side. However, the moisture content is also high in this region due to the rapid absorption of moisture through the grain surface. The results of analysis of the used solutions (Table VIII, line E) indicate that only about 0.1 per cent of NaCl passed through the epidermis.

6. *Hide treated for* 4 *days with saturated brine on grain side and distilled water on flesh side.*

Preliminary experiments with brine on the grain side for 24 hours showed very little salt penetration, consequently the length of the experiment was extended to 4 days. The results of analysis are shown in Table VI and Figure 7.

Examination of the data in Figure 7 demonstrates a moisture gradient which is low on the grain side and high on the flesh side, and a salt gradient

TABLE VI

Stratigraphic Distribution of Sodium Chloride and Water in Steer Hide Treated For Four Days with Saturated Brine on the Grain Side and Distilled Water on Flesh Side (Av. of Three Hides).

Stratum	Water	Sodium Chloride	Saturation
		Per Cent	
1 Epidermis	41.5	2.36	20.30
2	46.8	1.04	8.18
3	50.6	0.81	6.18
4	55.5	0.75	5.19
5	58.1	0.79	5.19
6	61.1	0.58	3.52
7	63.2	0.56	3.41
8	65.7	0.59	3.41
9	68.5	0.71	3.90
10 Flesh Side	70.4	0.67	3.52
Average	58.1	0.89	6.28

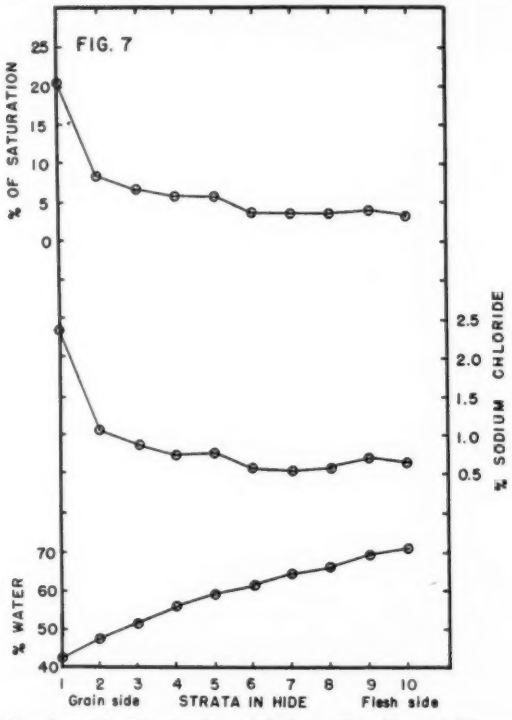

FIGURE 7.—Stratigraphic Distribution of Sodium Chloride and Water in Steer Hide Treated for 4 Days with Saturated Brine on the Grain Side and Distilled Water on the Flesh Side (Average of 3 Hides).

which is just the reverse. The result is that the greatest per cent of saturation is found in the epidermis and the upper part of the hair-follicle area. Part of this high salt content in the first two layers may be due to the salt in the hair follicles rather than to salt within the hide. The salt content in the lower six layers is actually less than that in the same layers in the fresh steer hide. This is due to the practically negligible salt absorption through the epidermis and the rapid moisture absorption from the flesh surface. The low moisture in the hair-follicle area is the result of strong osmotic forces of the concentrated brine in contact with the epidermis and in the hair follicles.

In Figure 8 the stratigraphic distribution of moisture after various experimental conditions is compared. In all cases the moisture in the corium is less than that of normal hide except when the hide is treated with distilled

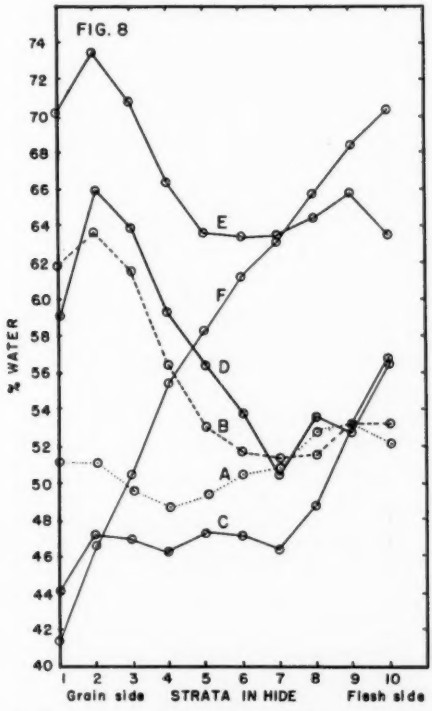

FIGURE 8.—Stratigraphic Distribution of Water in Steer Hide after Various Experimental Treatments. A, Saturated Brine on both sides for 4 days; B, Saturated brine on flesh side and distilled water on grain side for 24 hrs.; C, Saturated brine on both sides for 24 hrs.; D, Saturated brine on both sides for 4 hrs.; E, fresh steer hide; F, saturated brine on grain side and distilled water on flesh side for 4 days.

water on the flesh side, and salt on the grain side. This treatment results in a complete reversal of the normal moisture gradient.

Sodium chloride distribution after various experimental conditions is shown in Figure 9. Saturated brine on the grain side for 4 days (Curve E) does not change the salt concentration of the hide except in the epidermal area. This slightly higher salt concentration in the epidermal area is due to salt in the hair follicles themselves and to the very low absorption of some salt through the epidermis.

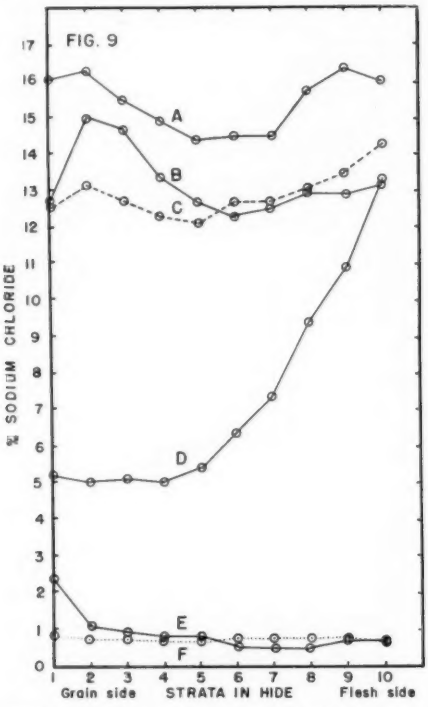

FIGURE 9.—Stratigraphic Distribution of Sodium Chloride in Steer Hide after Various Experimental Treatments. A, Saturated brine on both sides for 4 days; B, Saturated brine on flesh side and distilled water on grain side for 24 hrs.; C. Saturated brine on both sides for 24 hrs.; D, Saturated brine on both sides for 4 hrs.; E, Saturated brine on grain side and distilled water on flesh side for 4 days; F, Fresh steer hide.

7. *Analysis of Solutions.*

An examination of the data in Table VII, demonstrates that, when both sides of the hide are exposed to distilled water most of the salt and all of the soluble proteins which are removed from the hide leave through the flesh side.

TABLE VII

Analysis of Solutions Used in Studying Salt Penetration Into Hides.

Conditions	Time	On flesh or grain	Water	Sodium Chloride	Protein
			Per Cent		
A. Distilled Water on both sides	1 day	Grain	99.99	0.004	0.0
		Flesh	99.9	0.04	0.019
B. "	3 days	Grain	99.99	0.004	0.0
		Flesh	99.9	0.04	0.026
C. Brine on grain, Water on flesh	1 day	Grain	75.7	24.0	0.0
		Flesh	99.9	0.02	0.024
D. "	4 days	Grain	73.53	26.0	0.002
		Flesh	99.86	0.24	0.028
E. Water on grain, Brine on flesh	1 day	Grain	99.91	0.10	0.003
		Flesh	74.0	25.1	0.017
F. "	3 days	Grain	99.99	0.23	0.0
		Flesh	75.4	23.5	0.01

When saturated brine is placed in contact with the grain surface and distilled water in contact with the flesh surface for 24 hours, no protein is absorbed into the brine. About the same amount of salt and protein are found in the distilled water as in the previous experiment. However, after 4 days the salt passing into the distilled water on the flesh side has increased ten-fold and the soluble proteins have increased slightly. The total amount of salt which passed into the distilled water was 1.03 g. while the total salt present in the hide piece at the beginning was about 0.14 g. Since more salt was present in the distilled water than was present in the whole piece of hide, the additional salt must have come from the brine on the other side of the hide. This would definitely prove that salt slowly passes through the epidermis or grain surface, requiring several days.

When water is in contact with the grain surface and saturated brine with the flesh side, a small amount of salt penetrates through the epidermis to the distilled water in contact with the grain.

Conclusions

1. The stratigraphic distribution of Sodium Chloride and water in fresh and brined hides has been presented.

2. Moisture and salt in a fresh steer hide are present in greater quantity in the hair-follicle region than elsewhere in the hide.

3. Water passes very rapidly through the grain surface while salt diffuses very slowly.

4. Saturated brine penetrates a fleshed hide very rapidly (4 hours) when brined, or when treated with saturated brine on the flesh side.

5. A hide brined for four days shows a greater moisture and salt content than a hide brined one day.

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Discussion

A. N. Kay: This paper should be of interest to all of us in that it seems to indicate a desire on the part of the packer to obtain information which will indicate what takes place during curing, and so eventually enable him to give us better and more uniform hides.

There is one feature in which this work differs from commercial practice. That is, these hides were fleshed prior to treatment. The packers might achieve their goal, more easily, if they could persuade their employees that the flesh belongs on the carcass and not on the hide. This has been shown to be important by McLaughlin and Theis and other workers; the meat and flesh retard absorption of salt and make proper curing difficult.

There was one peculiar feature, to me, about this work, and that is that, after four days, there is an apparent gain in total absorption, and Dr. Strandine indicated that that was corroborated by an increase in the weight. I should like to know if he has any ideas as to why that increase should take place.

E. J. Strandine: The only explanation that we have is that when you first subject the hide to saturated brine, you have a rapid withdrawal of moisture from the hide, and a slow diffusion of salt into the hide. After a while an equilibrium is established between the salt concentration inside and outside of the hide. Then, for some reason, you have this slow up-take of both salt and moisture into the hide. We think it is partially due to the fact that collagen fibers and cells are partially going back to their normal shape. The brine is replacing the moisture that was present. We all know that brine has a higher specific gravity than moisture. Consequently, the hide should weigh more after it has completely taken up the brine than it did before. It is a case of replacing moisture with brine, and the brine weighs more than water. We

know that the hide has a final shrink, indicating that the fibers and cells do not completely regain their original size or weight.

R. L. STUBBINGS: I would like to make just a few comments on some of the observations that were made by Theis and McLaughlin back in 1922 and 1925, and some of the recent work on the practical curing studies as far as salt distribution goes that have been done in our laboratory. Theis and McLaughlin, of course, found that the epidermis was very resistant to penetration, and that penetration from the grain side only occurred after about one day in the limes.

Recently, we did some work on curing, on an entirely practical scale, on calfskin. The skins were cured in a standard way by packing down in salt, and we ran stratigraphic distribution of salt, moisture, protein and ammonium nitrogen in the packs after two, three, five, seven, and so forth, up to ninety days of curing. Now, that type of curing represents more what the tanner today finds in his hide cellar packs. It is not brined hide. It is hide that has not been fleshed, although on this particular group of calfskins the fleshing that had been done at the packing plant was extremely good. In this case, as differing from what Dr. Strandine has found from brining, we found that after three days of salt curing in the packs, the salt distribution had reached saturation as far as salt on water content goes, throughout the skin. That is, there was 26 per cent salt on moisture throughout the entire thickness of the skin after three days of the salt cure, and the same conditions held through the ninety-day cure, indicating that the pick-up of salt from a dry salt pack is fairly rapid and equilibrium of a sort is established within three days to a week. However, this rate of uptake may not apply on heavier hides, although steer hides that we have analyzed in the same manner from tannery-cured stock that has been cured, say two to three months, have demonstrated equilibrium conditions in the skin at that point.

I think Dr. Strandine's explanation of the apparent moisture regain probably is true, since it certainly does not represent a swelling—(if we consider swelling as an increase in the volume occupied by the protein) as everyone knows that if you salt cure a fresh skin, it decreases in thickness and consequently it cannot possibly be considered to swell. I believe that brining does the same thing as salt curing, that is, if you brine a piece of fresh skin, it decreases in thickness. I therefore think his explanation of the fact that you are just replacing water with a low density by salt of high density may help to explain the percentage increase that is found.

MR. JACKSON: The average hide buyer only knows three things. He knows he pays too much for hides. He never finds hides in the proper condition. And the hides are not properly cured. For that reason, it is quite necessary in our minds that a study be made on a better way of curing hides, a better way of curing them, not only to preserve them, but so that they can be shipped to the tannery safely with less moisture in them than they now have. We all realize what freight rates have done, and it is a rather costly

thing to have to pay freight on non-leather making materials.

Some of you may not know, that recently, through the suggestion of the American Meat Institute, a fund has been subscribed of $10,000 by the American Meat Institute, and $10,000 by the Tanners' Hide Bureau, which consists of just the cattle hides tanners, for study of a better cure, and in that study the American Meat Institute is undertaking the study of removal of manure before the hides go into the pack. One thing we are up against in the curing of hides, it seems to me, is that there is too much dirt and filth on the hair side and there is too much flesh and fat left on the flesh side. It appears to the layman that these two factors inhibit the rapid curing of a hide. It does not seem to us that with a lot of fat and flesh and manure on the hair side, the hides will cure as rapidly as they should. Therefore, the Tanners' Council have undertaken in the Research Laboratory at Cincinnati, the study of methods to improve the curing of hides. It is so important that we believe that any help that any of you technical men can give to the Laboratory in their research work will be quite welcome.

KAY: I think McLaughlin and Theis and the B.L.M.R.A. have shown that the pH of the brine has some bearing on the rate of absorption. Have you studied pH in this work?

STRANDINE: No, we did not investigate the effect of pH in this particular investigation.

P. R. SMITH: Since Dr. Strandine's paper showed the effect of the epidermis on the diffusion of salt, does he have any estimate of the effect of the flesh which is left on the hide on the diffusion of salt?

STRANDINE: I think it is well known that the flesh and particularly the fat will interfere with the diffusion of salt in the hide. A number of years ago, I reported at these meetings some experiments that we performed on brining of hides. We showed that salt diffusion into hides is quite rapid on fleshed hides, but it is greatly reduced by the presence of the fat or the flesh tissue. In the present paper, all the hides were fleshed to give a uniform surface, since the amount of fat on the hide is quite variable.

A Study of The Moisture Relationships and Thermal Properties of Skin and Leather

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The fundamental properties of animal skin collagen and leather are of interest to the tanner, the biochemist, and the ultimate consumer of leather.

*The material contained in this paper is part of a dissertation submitted to the Graduate School of Arts and Sciences of the University of Cincinnati by Seymour S. Kremen in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1949.

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Among these are the water-holding power of collagen and its thermal properties.

When one considers the subject of moisture in biological systems, the experimental data show that the properties of the water in the system are not those that one would predict for an equivalent amount of water in a free state. This anomalous behaviour is termed the "bound" water phenomenon.

"Bound" water may be defined as water which is associated with a substrate in such a manner that certain of its properties differ significantly from the measured properties of an equal amount of pure water.*

The measurement of many of the physical and chemical properties of water in diverse biological systems has yielded definite evidence for the existence of bound water. Gortner [9] has presented an excellent and comprehensive review of the subject.

In a great many instances, the uptake of water follows sigmoid adsorption isotherms of the Brunauer-Emmett-Teller [3] type, rather than stepwise stoichiometric relations such as are found in the hydrates of magnesium sulfate. This is taken to mean that at very low levels of moisture content, the bound water is relatively firmly held. Additional increments of water are progressively less firmly bound; while the exact amount of bound water is almost impossible to define sharply, the methods of measurement do indicate the approximate range where additional increments of water will exist in an essentially free state.

Gelatin gels have been extensively studied from the viewpoint of bound water [2 3]. Many of the conclusions obtained therefrom have been applied to collagen. Actual studies of the bound water behaviour of collagen and leather are less numerous. Bull [4] studied the water vapor adsorption of several proteins, including collagen. He found that they behaved as predicted by the Brunauer-Emmett-Teller equations for adsorption isotherms. Green [10] studied the water vapor adsorption of chrome tanned hide powder, and concluded that within the range of water uptake which is possible from the vapor phase, the affinity of water for collagen is not diminished by chrome tannage. Other authors who have studied the bound water phenomena in hide and leather include Eilers and Labout [7], Chesire and Holmes [5] and Compton [6].

The mechanism of the binding of water has been the subject of considerable speculation. There is substantial agreement that the binding is due to hydrogen bonds. The only direct evidence of the existence of such a link in a protein-water system, is that presented by Sponsler and co-workers [2 7] who reported the presence of the hydrogen bond in the infra-red absorption spectra of gelatin-water systems.

They also postulated that there are two types of hydrophilic groups capable of binding water in proteins. These are the polar side chains, and the oxygen

*Water of constitution is herein defined as water which is formed from atoms released by breaking of covalent bonds of an integral part of the protein itself, rather than the discrete molecular water which is thought to be hydrogen-bonded to certain centers on the polypeptide chains.

and nitrogen atoms of the peptide links. Pauling[25] studied the data of Bull[4] and concluded that the peptide groups had little water binding power. This was based on the data for nylon, which has no polar side chains, and also shows little or no water vapor adsorption. A referee who studied the paper, pointed out, however, that the close packing of the chains in nylon may be responsible for the failure of the water to penetrate. Pauling, using the best available amino acid analyses and the water vapor adsorption data of several proteins, found good agreement with his theory that the polar groups were responsible for the water binding of proteins. However, collagen and gelatin were unique, in that they did not show agreement on this basis. Pauling points out that these two proteins are also almost uniquely high in the secondary amino acids, proline and hydroxy-proline, and that their presence would liberate carbonyl groups of adjacent polypeptide chains, which would then be free to hydrogen-bond with water. The work of Mellon, Korn, and Hoover[20] with casein and glycine polypeptides is further evidence for this belief.

In this paper data are presented to show the relationship between the amount of water which may be removed from skin and leather and the thermal conditions which accompany the water removal. These data bear on the consideration of bound water in skin and leather, particularly at low levels of total moisture.

The removal of moisture from the skin protein and the exposure of the skin or leather to high temperatures produce important changes in the physical properties of the protein. Therefore it is essential that these changes be studied and evaluated concurrently with the moisture removal procedure. This was accomplished chiefly by a study of the changes in the shrinkage characteristics of the skin and leather which had been produced by the conditions of moisture removal.

Shrinkage temperature is utilized in a practical manner by the chrome tanner, and by the research worker as one measure of the stability of collagen and leather. There is a tendency among some research workers[11,18a] to use the shrinkage temperature as a universal criterion of leather quality, and to base all deductions of the tanning mechanism on the effects of experimental variables on the shrinkage temperature. There are several objections to this practice. The work of Weir[29] suggests that this phenomenon is a rate process such that small changes in conditions may significantly affect the measured result. The work of Theis[18] and others[15] indicates the profound effects of such experimental variables as salts, acids, and bases, various organic materials, and thoroughness of wetting on the measured value of the shrinkage temperature.

A further objection to the use of the shrinkage temperature as a universal criterion is the fact that experience has shown that elevation of the shrinkage temperature alone is not sufficient to guarantee good leather quality. Examples of this are to be found in the depression of the shrinkage temperature produced by oil tanning, and in the production of acceptable leathers[14] whose

shrinkage temperatures were not appreciably higher than that of raw skin. Vegetable tanned leathers of good quality may have an appreciably lower shrinkage temperature than a poorly tanned piece of chrome leather. In general there is a range of shrinkage temperature which is characteristic of the class of tanning materials used.

The effects of dry heating on collagen and leather, and shrinkage behaviour under dry conditions or in non-aqueous media have received little study. The general subject of dry heating and denaturation of proteins other than collagen has received more attention, and an excellent treatment of this subject is to be found in the work of Mecham and Olcott [19]. A comparison of their results, and those reported here for collagen, will be found in the discussion section of this paper.

Powarnin and Sapagonin [26] studied the influence of high temperature on the tensile strength of dry leather. They concluded that dry, untanned skin is most stable to dry heating, and that chrome tanned leather is the least stable. Green [10], on the basis of a change in the color of chrome tanned leather after heating, concluded that it was not heat stable in the vicinity of 100°C., possibly due to instability of the chrome complex. Kanagy [13] studied the evolution of CO_2 and water from vegetable tanned leather at elevated temperatures. His conclusions regarding vegetable tanned leather are obscured by inability to differentiate between protein degradation and tannin destruction. The results of a control experiment indicate that untanned hide powder is practically unaffected at 100°C. and only slightly decomposed at 140°C. Balfe and Humphreys [2] mention the effects of dry heating on leather, and the shrinkage temperature in oil. Since only unpublished data and private communications are cited as references, the significance of their data cannot be evaluated at this time. Lloyd and Garrod [15] mention that collagen has a shrinkage temperature of about 150°C. in glycerine. Their experimental conditions are not described.

Experience at this laboratory has indicated that the use of the conventional shrinkage tester [18b] for skin and leather which is in the dry state, or which has been degraded to some extent, is very unsatisfactory because of the relatively low sensitivity of the apparatus. Use of the conventional technique under such circumstances will reflect only gross changes, and the existence of significant changes of lesser magnitude may well be overlooked.

Theis and Serfass [28] have recently developed an electronic strain gauge for studying shrinkage behaviour which has provided a method for making this measurement with the necessary greater sensitivity. An electronic shrinkage meter was constructed at this laboratory. This meter was used to evaluate the relative thermal stability of untanned (depickled) and chrome tanned calfskin.

Experimental Methods

A. Determination of Total Water in Skin and Leather.

A necessary requirement for investigation of the water relationships of a system is a method for determining the total amount of water present. However, protein materials are very susceptible to degradation by heat and other methods of desiccation. Thus, it is not always possible to remove all of the water which is not water of constitution, without damaging the protein.

Many methods have been developed, and are in current use, to measure the amount of water in a protein sample. These empirical procedures give, if carefully used, reproducible, precise results of much practical value; however, they do no necessarily remove all the water, nor is protein alteration always avoided. Bull [4], Mecham and Olcott [19] and Gortner [9] have discussed and illustrated the limitations of some of the existing reference methods.

The problem of determining all of the water associated with a protein, without causing alteration of the protein, may be fundamentally incapable of solution, as the complete removal of bound water may leave the protein in a thermodynamically unstable state. A knowledge of the effects of experimental conditions and the determination of the extent of protein denaturation is therefore the best alternative.

The three principle methods for the determination of moisture are oven drying, the Karl Fischer technique [8a], and solvent distillation [8b]. The first method assumes that the loss in weight after oven drying is equivalent to the water content. Incomplete water loss and oxidative weight changes cause errors which may be minimized by vacuum drying, generally at lower temperatures. The Karl Fischer technique depends on the use of a specific oxidation-reduction technique involving iodimetry to titrate the water extracted from a sample by methanol. McComb [16] has pointed out that for use on proteins it is subject to a difficult manipulative procedure and to errors caused by incomplete water extraction.

In the solvent distillation procedure the sample is immersed in a boiling hydrocarbon from which the water and solvent are continuously distilled; the water removed separates in a calibrated receiving tube, which is read directly. This procedure, in comparison with vacuum oven drying, was used to study the moisture removal from depickled and chrome tanned calfskin because:

(1) The presence of the inert hydrocarbon atmosphere practically precludes errors due to oxidation.

(2) Accurate and automatic control of temperature is maintained by the choice of a solvent whose boiling point is suitable.

(3) The method determines only the amount of water which is removed. Any simultaneous weight loss other than water cannot cause an error. Loss of water of constitution will of course be reported along with water from any other source.

(4) Moisture removal as a function of time may be studied by frequent readings of the calibrated receiving tube. An oven procedure requires removal of the sample from the oven, cooling in a desiccator and weighing. After the samples are returned to the oven there is a lag period before thermal equilibrium is reestablished.

(5) The only disadvantage of the solvent distillation method is that it requires relatively large samples (10-15 gms.) for most accurate results. This was not a problem in the work at hand.

B. Measurement of Shrinkage Temperature Characteristics

The method selected to evaluate the thermal stability of calfskin was the measurement of the changes in the wet shrinkage characteristics which had been produced by dry heating under various conditions of time and temperature.

To secure the necessary sensitivity a wire resistance strain gauge and a suitable electronic amplifier, similar in principle to that described by Theis and Serfass[28], were constructed. A block diagram of the instrument is shown in Figure 1. The instrument operates on the principle that certain types of resistance wire undergo changes in electrical resistivity as a function of the mechanical force which is applied in the form of stretch or tension. The Wheatstone bridge technique is used to measure changes in voltage which are a linear function of the applied force.

The commercial gauge which was used in the instrument had a linear response in the range of 20-1300 gms. Changes of the order of one gram were detectable. By suspending known weights from the gauge the microammeter dial could be calibrated in grams or any other suitable units of force. Electronic controls incorporated into the amplifier circuit permitted the balance position and calibration to be rapidly and conveniently checked during operation. Little or no drift was observed if the instrument had been well warmed-up prior to use.

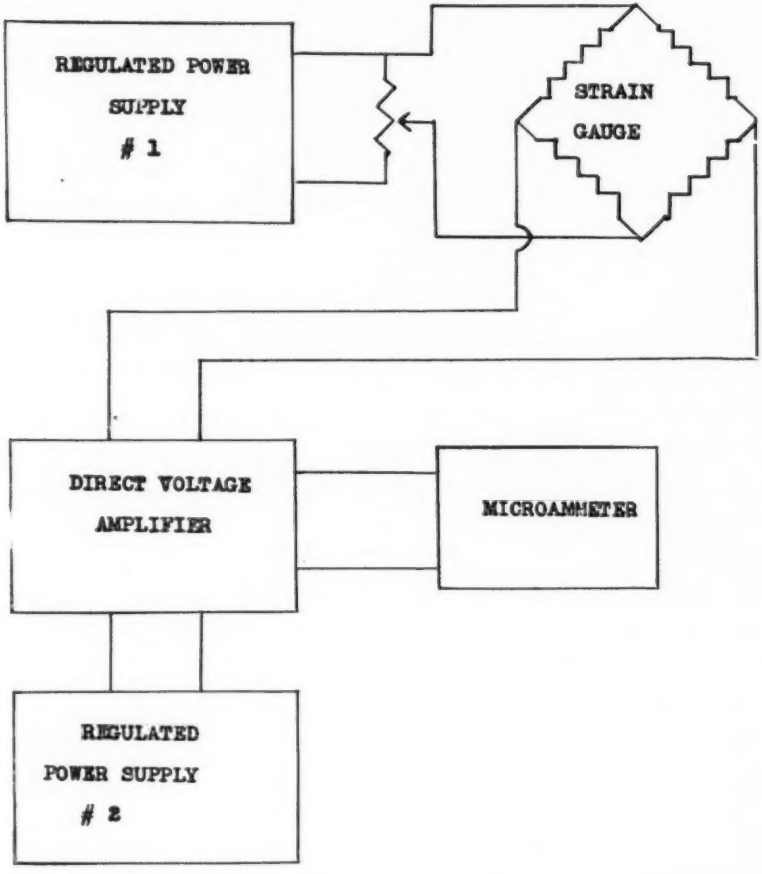
The instrument was equipped with a built-in electric stirrer and an immersion heater. The strain gauge was attached to the frame by means of a shaft which had a screw thread. One jaw of the sample holder was attached to the lower end of the gauge; the other jaw was rigidly fixed to the frame of the instrument. After the sample was fastened between the jaws, the screw thread was adjusted so that any desired initial tension could be applied. This was done to compensate for the elongation of the sample and consequent relaxation of tension that occurs as the temperature of the water is raised.

Samples (0.5 in. by 1 in.) were cut from pieces which had been split to a uniform thickness (generally about 0.060 in.). The samples were thoroughly soaked and wetted prior to the determinations. For samples of this size, an initial tension of 100 gms. was found sufficient to maintain a positive stress on the gauge at all times, and this tension was used for all the determinations.

FIGURE 1

BLOCK DIAGRAM -

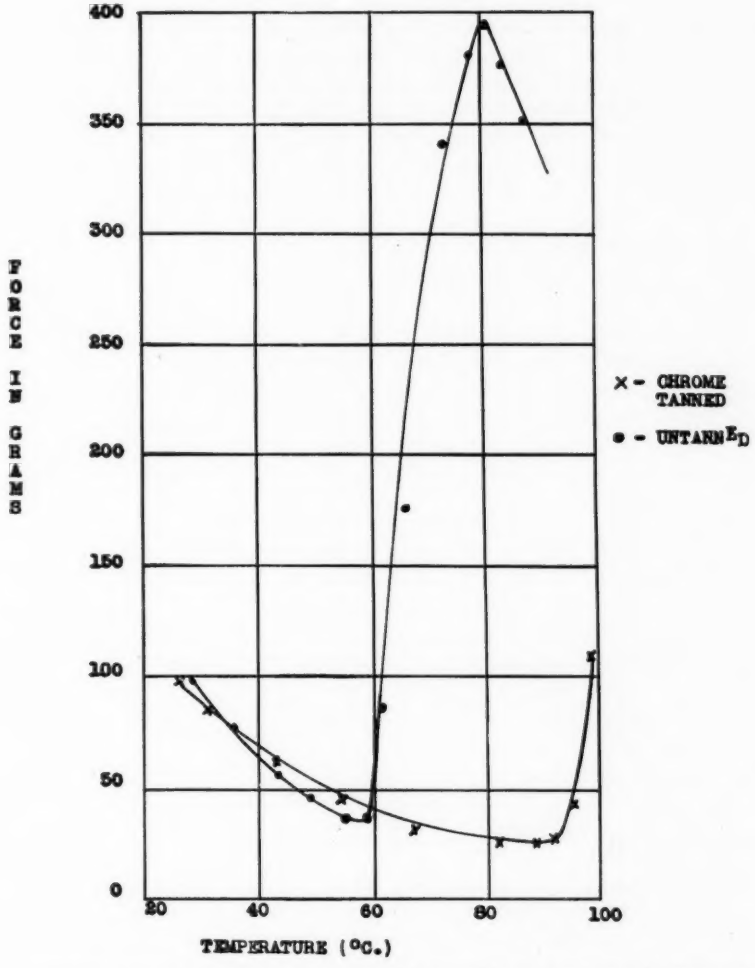
WIRE RESISTANCE STRAIN GAUGE AND AMPLIFIER



An initial tension of this magnitude did not appear to have any bearing on the final results. The rate of heating was set at 3°C./min. starting at room temperature in most cases. Severely degraded samples were hydrated in an ice and water bath, and the temperature at the start of the determination was between 2° and 5°C.

FIGURE 2

TYPICAL FORCE-SHRINKAGE CURVES IN WATER



Typical curves of data obtained by this procedure are shown in Figure 2. A study of the curve for untanned skin shows several phases of shrinkage temperature behaviour which are of interest:

(1) There is a relaxation of the initial tension, which gradually decreases to a relatively constant value.

(2) The tension remains at a relatively constant value for several degrees, and then begins to increase. The temperature at which the first increase is noted, is defined as the shrinkage temperature.

(3) Shrinkage, as evidenced by increasing tension, occurs at a rapidly accelerating rate for an interval of several degrees; then the rate of increase diminishes, and the tension again becomes fairly constant for an interval of 2-4 degrees; then a gradually accelerating relaxation is observed. The final relaxation marks the onset of gelatinization of the collagen. Gelatinization of chrome tanned pieces was not obtained under the experimental conditions which were used in this determination.

C. Tannage Methods

The untanned pieces were from commercial calfskins, which had been limed, bated and pickled. They were then washed free of acids and salts, and dehydrated by ethanol and acetone [12]. Half of each dehydrated skin was thoroughly soaked in water and chrome tanned in a drum, using sulfur dioxide reduced liquors whose basicity ranged from 27 to 33 per cent. The analytical data for these skins are to be found in Table I.

TABLE I

Calfskin Chemical Analysis – (Dry Basis)

	Untanned	Chrome Tanned
Lipid (Per Cent)	0.1	0.1
Ash (Per Cent)	0.1	3.48
Hide Substance (Per Cent)	100	92.5
Chrome Oxide (Per Cent)	0	3.23
Shrink Temp.	60°C.	93° C.
pH	5.35	3.36

Experimental Results

The solvent distillation procedure was applied to the determination of moisture in Standard hide powder, untanned and chrome tanned calfskin pieces. Samples were conditioned for one week or more at 70°F. and 65 per cent R.H.; they were then weighed into flasks and immediately covered with the various solvents. The solvents which were used had boiling points that ranged from 50° to 204°C. The determinations were run continuously for 4 to 5 days, and readings were made at intervals of a few hours during each day. The data obtained appear in Tables II and III and Figures 3 and 4.

TABLE II

Per Cent Water Removed from Standard Hide Powder
By Various Hydrocarbon Solvents Over a 4–5 Day Period

Solvent: B. Pt.	Cyclopentane 50°C.		Hexane (n) 69°C.		Methyl Cyclohexane 100°C.		Ethyl Cyclohexane 131°C.		Xylene 137°C.		Mesitylene 164°C.	
	Time Hours	Water Removed Per Cent	Time Hours	Water Removed Per Cent	Time Hours	Water Removed Per Cent	Time Hours	Water Removed Per Cent	Time Hours	Water Removed Per Cent	Time Hours	Water Removed Per Cent
	3	5.95	1	7.44	¼	6.58	1/6	8.57	1/6	9.08	1/6	9.33
	5	6.43	2½	8.65	½	7.98	½	9.74	½	10.21	¼	10.0
	6½	7.63	4	9.42	1	9.33	5/6	10.07	1½	10.69	1	10.91
	9	7.69	6	9.82	1½	9.75	1 1/6	10.17	2½	10.86	2	11.03
	12	7.69	7½	10.03	2	10.0	1½	10.27	4	10.99	4½	11.09
	23	8.05	16	10.63	3	10.37	3	10.43	6	11.1	5½	11.22
	26½	8.29	30	10.63	18½	10.73	3½	10.50	7½	11.28	7½	11.33
	31	8.35	43	10.72	20½	10.73	5	10.54	18	11.28	18	11.59
	47½	8.77	51	10.98	23	10.73	6½	10.59	20	11.28	19½	11.59
	49	8.77	67	11.03	25½	10.82	10	10.71	30	11.33	25	11.59
	53	8.98	74½	11.03	27	10.86	12	10.71	43	11.40	43	11.83
	55	9.13	79½	11.06	30	10.98	23	10.71	51	11.49	50½	11.94
	71	9.66	90½	11.08	32	10.98	26½	10.76	67	11.57	67	12.07
	76	9.72			44	11.10	27½	10.97	71	11.57	71	12.07
	79	9.72			47	11.10	31	11.19	75	11.57	74	12.07
	84	9.85			51½	11.1	47½	11.51	80	11.61	80	12.07
	95	9.85			68	11.21	49	11.31	90	11.63	90	12.13
	125	9.85			70	11.21	53	11.35				
					74	11.25	55	11.41				
					76	11.25	71	11.56				
					92	11.41	76	11.56				
					96½	11.41	79	11.56				
					99½	11.41	84	11.59				
							95	11.59				

TABLE III

Moisture Removed from Untanned and Chrome Tanned Calfskin Pieces after Boiling in Various Hydrocarbon Solvents

Equilibrium Attained after 4–5 Days. Initial and Final Nitrogen Content is Also Listed, in Those Instances Where They Were Determined.

Initial Nitrogen Content			Untanned Skin 149.7 mgm./gm.		Chrome Tanned Skin 136.0 mgm./gm.	
Solvent	B.Pt. (°C.)	Time Hours	Water Per Cent	Final N Content	Water Per Cent	Final N Content
n– Hexane	69	120	20.10	——	19.35	——
Benzene	80	120	20.35	——	19.60	——
Methyl Cyclo-hexane	100	100	20.40	147.5	19.83	135.8
Toluene	111	96	20.41	——	19.80	——
Xylene	137	96	20.58	——	19.88	——
Cumene	153	100	21.00	149.0	20.30	134.6

Table IV shows a comparison of results obtained by the solvent procedure, with those obtained by vacuum drying in ovens set at the same temperatures as the boiling points of the solvents. The significance of these results in regard to bound water will be discussed later.

TABLE IV

Moisture Removal and Nitrogen Checks as Function of Varying Drying Conditions—Calfskin Squares

Conditions	Time Hours	Water Removed	Nitrogen (mgm/gm) Initial	Final
		Per Cent		
Cyclopentane (B. Pt. 50°C.)	94	12.65	147.1	147.1
Vacuum Oven (50° C.)	96	12.91	147.9	147.2
Methyl Cyclohexane (B. Pt. 100° C.)	96	14.6	147.3	147.7
Vac. Oven (100° C.)	96	15.4	147.8	148.9
Cumene (B. Pt. 153°C.)	96	15.8	146.0	145.0
Vac. Oven (150°C.)	96	16.2	145.3	146.4

The next phase of the problem was to ascertain insofar as possible the extent of protein change which had occurred as a result of the drying procedure. It was noted that the untanned skin and hide powder tended to darken in color at temperatures above 100°C. This browning reaction was appreciable

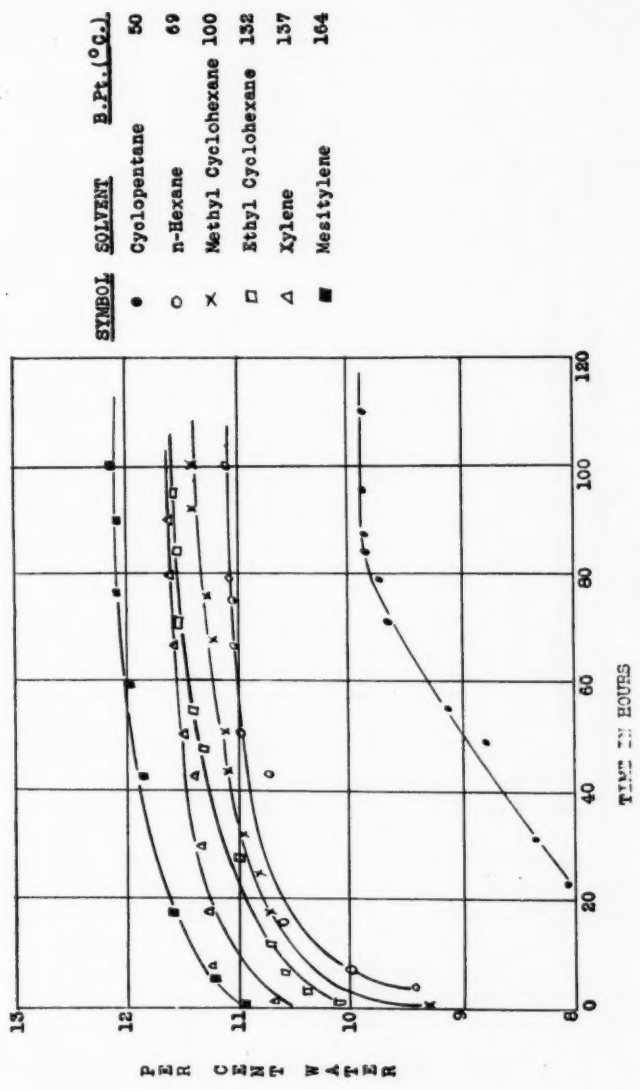


FIGURE 3

PER CENT WATER REMOVED FROM STANDARD HIDE POWDER BY VARIOUS HYDROCARBONS OVER A PERIOD OF 4 TO 5 DAYS

at the boiling points of cumene (153°C.). Significant decomposition and solubilization occurred at temperatures above 165°C. and the odor of nitro-

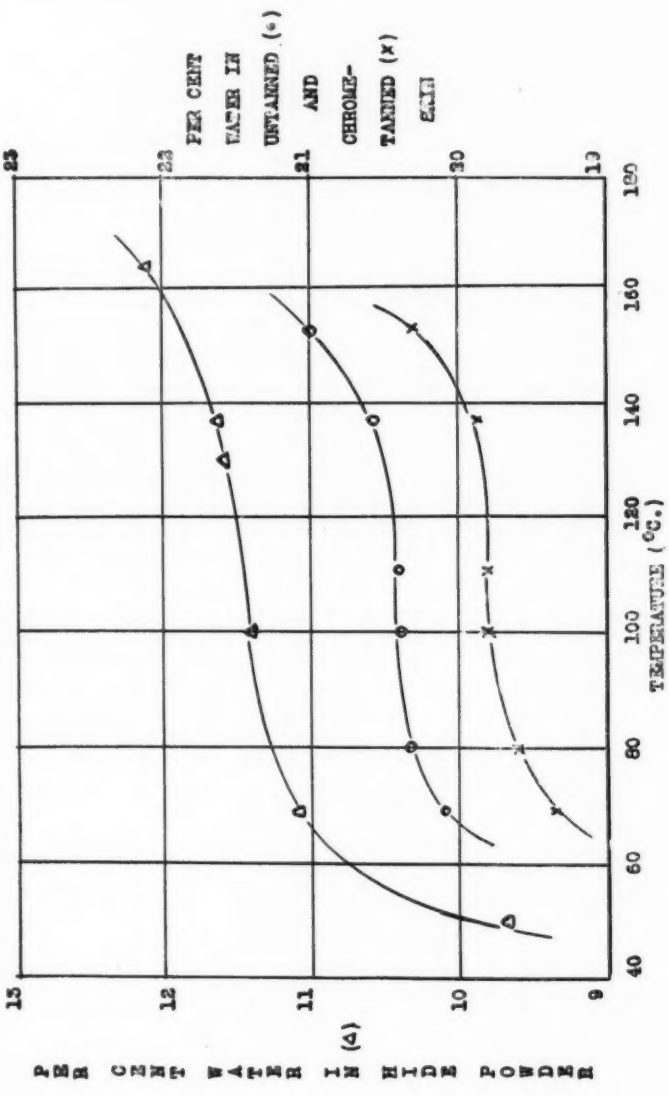


FIGURE 4

PER CENT WATER REMOVED AT EQUILIBRIUM TIME BY SOLVENT DISTILLATION FROM HIDE POWDER, UNTANNED AND CHROME TANNED SKIN AT VARIOUS TEMPERATURES

gen-containing degradation products was very pronounced. Increasing area shrinkage was also observed as the temperature was raised above 100°C.

A procedure was adopted to determine the amounts of nitrogen lost by the pieces in those cases where the decomposition was not apparent to the eyes and nose. Duplicate samples were run in conjunction with the moisture removal experiments. At intervals, pieces of known weight (which had been coded by punching a pattern of holes) were removed from the flasks. The pieces were immersed in absolute ethanol to remove the hydrocarbon; the alcohol was allowed to evaporate, and total nitrogen in the pieces was determined by the Kjeldahl procedure. The results obtained were compared with those obtained with unheated control pieces. The results of this procedure are shown in Tables III, IV and V.

TABLE V

Nitrogen Determinations to Check on Decomposition by Loss of Nitrogen from Hide Powder Under Various Drying Conditions.

Initial Nitrogen Content (mgm./gm.; as-is basis) – 161

Drying Conditions		Final Nitrogen Content (mgm./gm.) Original Basis
Boiling Hexane	24 Hrs.	162
Boiling Hexane	48 Hrs.	162
Boiling Hexane	72 Hrs.	160
Boiling Xylene	24 Hrs.	160
Boiling Xylene	48 Hrs.	163
Boiling Xylene	72 Hrs.	161
Air Oven – 100° C.	130 Hrs.	162
Vac. Oven – 70°C.	107 Hrs.	160
Vac. Oven – 140°C.	106 Hrs.	161
A.L.C.A. Evaporator	26 Hrs.	160

In addition to the study of the chemical decomposition of the protein induced by heating, information was obtained about the physical changes that occurred by studying the changes in the wet shrinkage characteristics which were produced by dry heating. The procedure employed was essentially the same as that used to study the nitrogen losses. Pieces were removed from the flasks at intervals, immersed in absolute alcohol to remove the hydrocarbon, and then soaked in water until thoroughly rewet. Their wet shrinkage temperature curves were then determined on the instrument which has already been described. The salient characteristics of the curves are reported in Table VI.

It was also deemed worthwhile to obtain information regarding the shrinkage behaviour of skin and leather under anhydrous condition. Paraffin oil (100 second viscosity, U. S. P. grade) was used as the heat transfer medium. The pieces were air dry. Some determinations were made on dry samples which had been brought to about 2 per cent moisture in the vacuum desiccator

TABLE VI

Changes in the Wet Shrinkage Temperature of Untanned and Chrome Tanned Pieces Produced by Heating in Various Hydrocarbon Solvents at the Boiling Point for Periods of 4-5 Days

Time Hours	Untanned+			Chrome-Tanned*+
	Shrink. Temp. (°C.)	Temp. of Max. Force (°C.)	Max. Force (gm.)	Shrink. Temp. (°C.)
		n-Hexane – B.Pt. – 69°C.		
2	59.5	82	575	91
5	60	85	800	92
22	59	85–89	1000	88
46	59	86–88	1240	88
70	59	84–87	425	88
94	60	85–88	850	84
		Benzene – B.Pt. – 80°C.		
2	60	81	395	87
5	60	86	750	87
22	59	85	510	77
46	60	89	1390	79
70	59	83–Boil	1270	87
94	58	92	595	79
		Methyl Cyclohexane – B.Pt. – 100°C.		
1	60	82–88	900	77
3	60	84	745	74
19	56	86–88	535	69
43	56	**		66
68	55	**		64
100	55	**		
		Toluene – B.Pt. – 111°C.		
1	58	80	510	82
4	58	91	1025	74
12	58	93	825	66
28	56	**		64
52	53	**		59
72	52	**		42
96	52	**		42
		Xylene – B. Pt. – 137°C.		
1	56	90–98	850	64
4	50	**		44
12	48	**		46
27	31	**		37
52	23	**		22
72	22	**		22
96	14	**		22
		Cumene – B.Pt. – 153°C.		
1	52	**		42
3	44	**		22
8	32	**		27
19	21	99	830	19
43	9	Boil	1065	15
68	4	**		12
96	4	95–Boil	700	17

*No maximum ever observed in water for Chrome Tanned Skin.
**No maximum reached up to B.Pt. of H_2O.
+Shrink. Temp. of Controls – 60° and 93° C., respectively.

at room temperature. The results were the same as those for the air dry samples. Ethylene glycol was used as the heat transfer medium in one instance to check on the validity of the results obtained with the paraffin oil. Determinations were made on the untanned and chrome tanned calfskin pieces which were used for the previous experiments, on a commercially chrome tanned mechanical leather containing more than 10 per cent chromic oxide on the dry basis, and on raw and chrome tanned kangaroo tail tendon fibers. All determinations were made with the electronic force shrinkage-meter. The results are shown in Table VII.

TABLE VII

Comparison of Wet and Dry Shrinkage Temperatures

Sample	Shrinkage Temperature (°C.)		
	Water	Mineral Oil	Ethylene Glycol
Untanned Calfskin	60	92	—
Chrome Tanned Calfskin	93	92	—
Chrome Tanned Mechanical Leather	Above 100*	92	92
Untanned Tendon Fiber	54	52	—
Chrome Tanned Tendon Fiber	91	51	—

*Unaffected by 10 minutes in boiling water.

Discussion

The results obtained from the solvent distillation method (see Tables II, III, IV, V, and VI) have provided information about the effect of heat, time and chrome tannage on the removal of moisture from hide substance. Figure III shows that when the determinations were sufficiently prolonged (4 to 5 days) an equilibrium condition is reached at any one value of temperature as determined by the boiling point of the solvent. The amount of water removed at this equilibrium time is a function of the temperature which prevails. The higher the temperature, the greater is the amount of water which is removed. Similar behaviour has been observed for other proteins [2 4].

Figure 4 relates the amounts of water removed at equilibrium time with the temperature of removal. The data indicate that bound water exists at the low levels of moisture under consideration (i.e. the final 1 to 2 per cent water which remains in the skin after conventional drying procedures at 75 - 100°C. overnight). The methods employed did not permit any conclusions as to the amount of bound water at higher moisture levels. The curves indicate that there are gradations in the strength of the binding, as additional increments of energy are required to remove additional amounts of water. The similarity of the shape of all three curves, and in particular the similarity of the curves for untanned and chrome tanned skin pieces, suggests that this

is a characteristic property of the hide substance, and that it has not been affected by chrome tannage.

Additional confirmation of such an interpretation is available from the data in Table IV. Comparisons were made of the amounts of moisture removed by solvent distillation with the amounts removed by the use of vacuum ovens maintained at the same temperatures as the boiling points of the solvents. The observed behaviour was similar with regard to the effects of increased temperature. However, in all cases, slightly larger amounts of water were removed by the vacuum oven than by the solvent at the same temperature. This is probably due to the fact that the vacuum oven combines a temperature effect with a pressure differential, with the result that effectively more energy is supplied for the water removal mechanism.

The validity of the above conclusions is dependent on the assumption that any water which is removed is not water of constitution, but discrete molecular water only which is associated in some manner with the hide substance. It is reasonable to believe that protein degradation which would liberate the elements of water by breaking of covalent bonds would also be accompanied by a loss of nitrogen. Tables III, IV and V contain data concerning the amounts of nitrogen which were present at all stages of the various heating procedures. In no instance was any loss of nitrogen observed. The data show results for temperatures as high as 153°C.; and actually there is no significant loss of nitrogen up to temperatures as high as 160 - 165°C. (boiling mesitylene). At temperatures in the range of 175 - 200°C. there is obvious decomposition, with profuse volatilization of nitrogenous degradation proproducts. Kanagy [13], who studied the loss of carbon from hide powder, found that there is little loss of carbon at temperatures as high as 140°C. Further confirmation may be found in the work of Mecham and Olcott [19]. They studied the effects of dry heating on a number of proteins (collagen and gelatin were not included) and found no loss of nitrogen up to 153°C.

The results which have been presented, and the literature that has been cited, substantiate the conclusion that the moisture which was removed from the hide substance was not water of constitution. However, the hide protein was not unchanged by the heating procedures. At temperatures above 100°C. area shrinkage was observed, and it appeared to increase with rising temperature. At temperatures in the region of 140°C. a certain amount of browning was observed in the hide powder and untanned skin pieces (the color of the leather would obscure any such manifestation in the chrome tanned pieces). At higher temperatures, particularly above 175°C. this browning is very pronounced.

The procedure used to study the extent of changes other than chemical decomposition, was the measurement of the wet shrinkage temperatures. The results in Table VI compare the values of the wet shrinkage temperatures of skin pieces; the variables are time, temperature and chrome tannage.

The salient features of these data are:

(1) Chrome tannage decreases the stability of dry hide substance to thermal change. Chrome tanned pieces exhibit reductions in wet shrinkage temperature when heated in the dry state at temperatures as low as 60°C. Raw pieces are relatively stable at 100°C. At all temperatures up to 140°C. the wet shrinkage temperatures of chrome tanned pieces are lowered more rapidly and to a greater extent than those of the untanned pieces. The instability of chrome tanned leather to dry heat which was observed is in agreement with the conclusions of Powarnin[26] and Green[10] which have been mentioned previously.

(2) The action of heat on the untanned hide substance seems to produce a resistance to gelatinization. The results noted in the column entitled "Temp. of Max. Force" (the temperature at which gelatinization commences) show that as the temperature of heating is raised, the untanned skin requires progressively higher temperatures for gelatinization. At any one temperature, increased time of heating also raises the temperature of gelatinization. This is definitely the case for temperatures up to 140°C. The results for cumene (B. Pt. - 153°C.) suggest that a maximum value for this effect may have been reached.

The results of the determinations of the shrinkage temperatures in non-aqueous media were shown in Table VII. The wet shrinkage results are also shown for purposes of comparison. The significance of these results lies in the fact that chrome tannage has produced no change in the dry shrinkage temperature. In a few instances other workers have measured shrinkage temperatures under non-aqueous conditions. The results of Meyer[21] and his associates with tendon collagen indicates that the dry shrinkage temperature is in the neighborhood of 120°C. Lloyd[15] mentions that the shrinkage temperature in glycerin is in the region of 150°C. The lower values reported in this paper are very probably due to the greater sensitivity of the electronic instrument which was used for this work. In all instances where a comparison has been made, the shrinkage temperatures obtained by the use of the official instrument[18b] have been appreciably higher than those obtained by the new electronic instrument. The differences varied in magnitude, depending on the type of material and the medium in which the measurement was made.

In any event the important factor is the comparison between untanned and tanned materials, and between skin collagen and tendon collagen. Inasmuch as the same instrument was used for all materials, the comparison on the basis of changes due to tannage and different media is valid. In the absence of additional evidence from other methods of judgment it is not yet possible to completely and finally reconcile, in terms of the mechanism of tannage, the wet shrinkage temperature behaviour with the dry shrinkage temperature behaviour. A reasonable hypothesis may, however, be offered.

An increasing hydration, which finally results in a probable rupture of forces holding polypeptide chains in a certain configuration, accompanies the shrinkage temperature effect in water. This hydration results in a swelling and elongation of the collagen which is quite noticeable just prior to shrinkage. When the determination is carried out under inert non-aqueous conditions, the shrinkage which is observed is due to purely thermal effects. These facts, and the results obtained, suggest that the shrinkage which is observed in water is actually a net effect of two or more individual effects which are occurring simultaneously at different rates. In the case of untanned skin, hydration sufficient to rupture the forces linking the polypeptide chains and permit reordering of the chains occurs at a temperature at which the reordering due to purely thermal effects is occurring at a negligible rate.

Baker[1] has discussed this reordering of chains in systems of synthetic polyamides, and presents X-ray evidence which contrasts the relative rates of reordering with paraffin oil and water at 100° C. The effect of the water is very much greater. In the case of the chrome tanned skins the hydration which precedes reordering presumably occurs at a lower rate than that of raw skin, and a considerably higher temperature is required to hydrate the leather to the point where rupture and subsequent shrinkage will occur. If the reordering due to purely thermal effects is unchanged and proceeding at a constant rate, its effect will be overshadowed by the swelling and elongation which is occurring simultaneously. This hypothesis therefore accounts for the apparent anomalies between the wet and dry shrinkage temperatures of untanned and chrome tanned skin.

There still remains to be explained the fact that the wet shrinkage of chrome tanned skin is so much greater than that of untanned skin. Lloyd and Garrod[15], on the basis of Speakman's criteria for evaluating relative porosity at *molecular dimensions*, conclude that collagen has a relatively open structure. McLaughlin, Cameron and Adams[17] have postulated that chrome tannage is due to the physical deposition of the $^2/_3$ basic chrome sulfate in and around the collagen fibers. From these considerations it might be postulated that one of the actions of chrome tannage is to reduce the porosity, and thus greatly reduce and hinder hydration. This would explain why higher temperatures and longer times are required to hydrate chrome tanned skin to the point of interchain rupture.

The views of Meyer[22] on the mechanism of the shrinkage of collagen might also be used to explain the changes in wet shrinkage temperature which are produced by tannage. He regards wet shrinkage as a "two-dimensional solution of the crystallites in the water of imbibition". It is perfectly conceivable that the presence of the tanning materials would alter the solubility properties so that the observed change in wet shrinkage would occur. This mechanism of wet shrinkage would not necessarily disturb the picture for the purely thermal reordering which occurs in anydrous conditions.

There is implicit in the foregoing considerations and conclusions the belief that shrinkage temperature is a rate phenomenon. Everyday experience in the plant and the laboratory where shrinkage temperatures are determined supports this view. More formal support is available in the papers of Weir[29]. All the results which have been presented in this paper were obtained under conditions where the rate of heating was standardized in order to minimize any variations due to this factor.

All of the experimental measurements which have been made in this work have indicated that chrome tannage has produced no significant alteration in the water binding power or dry shrinkage temperature of skin collagen. The results are more readily reconcilable with a theory of physical deposition in the manner postulated by McLaughlin[17] than they are with a strictly chemical theory of chrome tannage. This also applies to the observed thermal instability of the chrome tanned skin below 100°C. Changes at such a low temperature are unlikely to be due to changes in the chrome complex. They suggest some disaggregation or disordering of the collagen. Again, that is not inconsistent with a theory of physical deposition, nor with the considerations of porosity which have been discussed. Further, if Pauling[25] is correct in concluding that all of the polar side-chain groups in collagen bind water, then the fact that chrome tannage has not affected the water-binding power could indicate that chrome tannage does not involve the polar side chains.

Summary

Methods have been developed for the study of the effects of heating and moisture removal on the chemical and physical properties of untanned and chrome tanned hide substance.

The experimental results may be summarized as follows:

(1) The conditions and effects surrounding the removal of water from hide substance by the action of heat have been demonstrated.

(2) The existence and nature of bound water in skin and leather under specified conditions has been demonstrated.

(3) Shrinkage temperature studies have indicated the relative heat stability of untanned and chrome tanned skin. Dry shrinkage temperature studies have demonstrated that chrome tannage does not alter the collagen in this respect.

(4) The bearing of the results on possible mechanisms of shrinkage temperature and chrome tannage has been discussed. A hypothesis has been offered to explain the results which have been obtained. This hypothesis is not inconsistent with the physical deposition theory of McLaughlin[17], which was based on stoichiometric considerations concerning the fixation of the chrome tanning compound by the hide substance, but it does not preclude the possibility of some chemical union of the skin protein and the chrome tanning material.

Acknowledgment

Acknowledgment is made to the Tanners' Council of America whose support made this work possible. Thanks are also extended to the Director and Staff of the Tanners' Council Laboratory for their aid and counsel throughout the course of the work.

Addendum

A reviewer has expressed disagreement with the conclusions regarding the mechanism of chrome tannage. He specifically points out that the viewpoint of the authors is inconsistent with the work of Bowes and Kenten, [*J. Intern. Soc. Leather Trades' Chemists*, **33**, 367 (1949)], who attributed chrome tannage to the penetration of the chrome complex by the carboxyl groups of collagen. The reviewer also asserted that the chrome complexes are capable of binding water and that they could probably make up for any loss in water binding power of collagen resulting from chrome tannage. He further asserted that there was a definite likelihood that the explusion of these aquo groups from the chrome nucleus could occur at or below 100°C. and that the instability of chrome tanned leather on prolonged heating might possibly be due to the action of acid.

The authors have not attempted to use the results of this experimental work to definitely establish any one theory of chrome tanning, but have felt it necessary to point out which of the existing viewpoints appeared to most logically consistent with the experimental results. Bowes and Kenten obtained maximum (but not total) inhibition of chrome tannage by using collagen which had been methylated by the use of dimethyl sulfate. Experience at this laboratory has shown that the use of this reagent causes severe degradation of the collagen. Bowes and Kenten themselves [*Biochem. J.*, **44**, 142 (1949)] state that the use of dimethyl sulfate produces a "methylated" collagen which is badly swollen, discolored and odoriferous, and with a greatly increased soluble nitrogen content when washed at pH values as low as 9. They also were unable to analyze for the amount of methyl groups attached to nitrogen, which might have had a significant bearing on chrome tanning potential. Bowes and Kenten assigned all of the values for methoxyl to the esterification of carboxyl groups. The question might also be raised as to the possibility of the methylation of the hydroxy groups of hydroxy proline. The authors feel that any conclusions based on such an obviously altered material as this "methylated" collagen must be extremely judiciously considered, and that such conclusions alone are therefore insufficient to establish a mechanism of chrome tannage for unaltered collagen.

The authors feel that the question of alterations in the chrome complex at temperatures below 100°C. is still an open one. It is felt, however, that any changes are not due to the loss of water. Pierce [*J. Am. Leather Chemists Assoc.*, **37**, 547 (1942)] prepared the $^2/_3$ basic chrome sulfate. This salt has a

theoretical water content of 35 per cent. Pierce found that by drying to constant weight of 230°C. he was able to account for the theoretical amount of water, but that at temperatures well below this value the loss of water was very slight and slow. The role of acid in the heat deterioration of chrome leather may well be worthy of further study.

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ABSTRACTS

Note on Various Methods for Determining Extent of Coordination to Trivalent Chromium or Organic Anions. By S. G. Shuttleworth. *J. Soc. Leather Trades' Chemists*, **34,** 3 (1950). The author examined three methods for determining the degree of penetration of organic anions into chrome complexes. Aqueous solutions of chrome alum were boiled with sodium acetate after which the three procedures were applied. These were (1) direct estimation of non complex bound acetic acid and acetate by means of ether extraction, (2) determination of ionic sulfate by the benzidine hydrochloride method and (3) determination of penetration by conductimetric titration. From his results the author concluded that the solvent extraction method is limited to estimation of monofunctional molecules such as monobasic acids. The ionic sulfate method is not to be recommended as the sulfate liberated is the result of three equilibria, namely, rapid hydrolysis of complex bound sulfate caused by the alkaline salt, followed by replacement of sulfate by organic anion, and finally readjustment of ionic and nonionic sulfate to a new equilibrium. The conductimetric method may fail to distinguish between free weak acid and the complex, and any flat initial portion of the alkali curve must be taken as indicating the probable titration of free acid over this region, but this weakness in the method does not detract seriously from its usefulness in following ionic mobility changes and the reaction of complexes with alkali and acid. Potentiometric and spectrophotometric methods are discussed briefly and their limitations pointed out.

Some Causes of Variation in the Composition of Fish Oils. By J. A. Lovern. *J. Soc. Leather Trades' Chemists*, **34,** 7 (1950). General features of fish oils in comparison with oils from land animals and plants are discussed. Fish oils are characterized by the large number of fatty acids present, and by the presence of unsaturated derivatives occurring, over most, if not all, of the range of molecular sizes of fatty acids present. The compositions of aquatic animal fats, the influence of dietary fat, temperature, salinity, and selective mobilization, and selective distribution within the animal are shown in tabular form and discussed. It is shown that a genetic factor, traceable to differences in the animals' evolutionary history can cause the most profound of all the differences in fat types, but certain species do not exhibit any effects clearly attributable to it. Dietary influence on fat composition may sometimes be important. The general tendency is for the animal to lay down a depot fat resembling its dietary fat. Lowering temperature tends to increase the degree of unsaturation in the fat. Salinity is responsible for two distinct average fat types characterizing fresh water and marine fish, respectively. It appears to operate on the lowest links in the food chain, possibly on the plankton crustaceans, and the effect may be a dietary one for the larger species. Selective mobilization sometimes seems to take the form of a more ready utilization of smaller molecules when fat is withdrawn from the depots. Selective distribution of the total fat within the animal seems to operate on a basis of molecular size, and may produce quite marked modifications. The six factors given may operate in almost any combination.

Vegetable Tanning IV. Effects of Salts of Strong Acids. By D. Burton and J. M. Harrison. *J. Soc. Leather Trades' Chemists*, **34**, 21 (1950). Mimosa liquors of 50°Bk. were acidified to pH 3.5 with formic acid and then reduced to 30°Bk. To these liquors 0,20,40, 60, and 100 mgm. equivalents of sodium chloride were added, hide tanned therein, and examinations made of liquors and leathers after 10 and 34 days, respectively. These observations led to the following conclusions. Speed of penetration increased with increasing addition of salt, but there was no corresponding fall in tannin content of the liquors. Higher salt concentration led to softer leathers. Plumpness increased and drying speed decreased with increasing salt in the liquors. Yield was not appreciably affected. pH of the liquor decreased slightly with increasing salt concentration. Salts of weak acids increased. Salt had a greater effect on the rate of tannin fixation than on the tannin fixed. pH value of the water solubles and shrinkage temperature of the leather decreased with increasing salt content of the liquors.

The Importance of pH Value and of the Concentrations of Salts and of Acids in Vegetable Tanning. By M. P. Balfe. *J. Soc. Leather Trades' Chemists*, **34**, 30, (1950). The author discusses the importance of acid and salt concentration and pH of tan liquors with respect to tanning and leather characteristics. Recommended limits for salt and acid contents in milligram equivalents per liter are shown in the following tabulation:

	Heavy Leather		Medium Strength Tannage	Light Leather	
	Sole or strap butt, over 100° Bk. in strongest liquors		Dressing hides 30-70° Bk. in strongest liquors	Sheepskins Below 30° Bk.	
	Hot Liquor	Cold Liquor		Bated Skin	Pickled Skin
pH	3.0–4.5	3.0-3.5	3.8–4.5	3.5–5.0	not below 3.0
Salt Content	150–250	200–300	75–125	20–70	about 300
Acid Content	Decreasing steadily from strongest to weakest liquor and below 20 in spent liquor				

The Effects of Humidity on the Air Permeabilities of Leathers. By R. G. Mitton. *J. Soc. Leather Trades' Chemists*, **34**, 41 (1950). There are two methods for measuring specific surface of leather which are measurement of the adsorption of an inert gas at low temperatures, and measurement of the permeabilities of specimens to gases. In the adsorption method it is difficult to control the moisture content of the fibers while cooling them to the low temperature of approximately–183°C. at which measurements are made. If the leather is completely dried out first, the fibers shrink and the fibrils are probably separated thereby or else cohere, so that the specimen is not the same as in the beginning.

In adopting the permeability system, the U-tube apparatus was considered. The specimen was clamped in the device so as to assure no leaks and air then passed through the leather at low pressure. A description of the apparatus is given in detail. A difficulty encountered in the measurement of the air permeabilities of leather specimens is that their values depend to quite an extent on the pressure differences between opposite faces, probably attributable to distention of the specimens with consequent distortion of the capillary channels through them. As a result, permeabilities were found to differ with flow of air from or toward the grain or flesh side of the specimens. To reduce distortion to a minimum pressure differences should be kept as low as possible when making measurements. Even with pressure as low as 1 cm. of water, a light chrome calf leather of 0.92 mm. thickness

showed the effects of distention by (1) permeability increased with increasing pressure difference with no indication of a constant value as the difference between faces was reduced; (2) a higher permeability when directional flow of air was from flesh to grain. The U-tube method was discarded in favor of equipment wherein comparison was made of resistance to gas flow of the specimen with the resistance of a pair of calibrated capillary tubes through which the same gas stream passes. A description of the apparatus is given. Permeability measurements of several leathers are shown in graph form. Permeability was found to decrease with increasing relative humidity, and is explained by the swelling of the fibers with rising humidity. The nature of the leather itself has a bearing on the magnitude of the change in permeability with humidity, as for example, vegetable tanned leather showed 70 per cent decrease in permeability as the humidity changed from zero to 93 per cent. Chrome leather decreased only 55 per cent. No relationship was found between the shapes of the permeability-humidity and absorption-humidity graphs. Permeability measurements on oiled and subsequently degreased specimens gave no evidence of decided difference brought about by the degreasing.

Directional Variations in Strength and Stretch in Calf, Goat, and Sheep Leather. By G. O. Conabere and R. H. Hall. *J. Soc. Leather Trades' Chemists*, **34,** 57 (1950). Vegetable tanned sheep, chrome tanned goat, and chrome tanned calf leathers were examined for tensile strength and stretch. It was found that samples cut at any particular area in the direction of the hair growth showed higher tensile strength and less elongation at break than like-positioned samples cut at right angles to the hair growth. Greatest tensile strength was found in the back bone and in the tightly woven back areas. Neck, and belly and shank edges showed the least strength. Directional differences were greatest and most consistent in the calf leather. The goat leather was the most uniform in average strength in the different directions but varied considerably in stretch. Differences found between the three types of skin were regarded as probably inherent in them and due to their fiber structure, but possibly affected by different methods of curing, tanning and drying in process.

A Comparison of Tensile and Tearing Tests for Light Leathers. By R. G. Mitton and R. H. Hall. *J. Soc. Leather Trades' Chemists*, **34,** 66 (1950). Chrome, semichrome, vegetable and oil tanned leathers from sheep, calf, kid and goatskins, and splits from horse and cow hides and sheepskins were subjected to tensile strength and tear tests. In addition, three of the vegetable tanned leathers were subjected to damage by excess acid and wet heat, respectively. The authors summarize their findings as follows: The results of different kinds of tear tests on a series of leathers are compared with one another and with the results of tensile strength tests. Although a strong leather is likely to offer high resistance to tearing, the results show that tear and tensile tests are not merely measurements of the same property, expressed in different units, but tensile breaking loads and tearing loads are to a certain extent independent of one another. Linear tear tests and buckle tear tests, however, appear to measure essentially the same property, while a stitch tear test appears to be intermediate between a tensile test on the one hand, and a buckle tear test on the other. The results of tensile tests of a leather depend to a marked extent upon the directions in which the specimens are cut, but buckle tear tests show much less dependence on direction. These conclusions may be explained in terms of the fibre weave pattern in leather. The question whether a tear test forms a specially sensitive criterion of damage is examined. The results of experiments using vegetable tanned leather samples, damaged by excess acid or by heat, show that, for such material at least, a tear is no more sensitive than a tensile test.

Some Physical and Chemical Properties of Vegetable Tanned Belting Leathers. By R. G. Mitton. *J. Soc. Leather Trades' Chemists*, **34**, 81 (1950). The author conducted extensive experiments to discover what physical and chemical data would be useful for assessing the quality of vegetable tanned butts, especially their strength. From the experiments certain conclusions were reached, as follows: (1) The chemical analyses showed no exceptional features. The most noteworthy point is the considerable variations of the acid values of grease extracted from the curried butts. This may be attributed to the hydrolysis of grease by microorganisms present in the leathers. (2) The tensile strengths of dry, wet, and curried specimens from the Official sampling position and from the shoulder range demonstrate that:- (a) Some tanneries produce stronger leather than others; the differences are not attributable to sampling variations. (b) Wetting or currying the leather increases its strength, and on the average by about 17 per cent. (c) Leathers from some tanneries respond more than others to wetting or currying. If the tensile strength of curried leather from a particular tannery is required, it must be found from measurements made on the leather after currying; it cannot be deduced from other measurements. (d) The specimens from the shoulder range are stronger than those from the Official position. (e) Some tanneries obtain high values for strength at one sampling location without attaining correspondingly high values at the other. (f) The increase of strength caused by wetting or currying is greatest for specimens from the shoulder range. (g) There is no evidence that a currying process that is good for one leather is not good for all. (3) The corresponding data for elongation at break show that: (a) Some tanneries produce leather with greater extensibility than others. (b) There are real differences between the elongations of dried, curried, and wetted leathers, and they increase in that order. The lubrication of fiber surfaces at places where they are in contact is not the only function that the water or grease performs. (c) Butt specimens are less extensible than specimens from the shoulder range. (d) Wetting or currying increases the extensibilities of some leathers more than others. (e) The elongations of specimens from the shoulder are for some tanneries higher, and for some tanneries lower than would be expected from a consideration of the elongations of the butt specimens. (4) Tensile strength shows some correlation with hide substance content, and hence also with other chemical factors that are necessarily correlated with hide substance (for example, fixed tan and water-solubles). There is little evidence otherwise that, in the range covered by the experiments, the strength of elongation is related to chemical composition. (5) For butt specimens there is some correlation between tensile strength and elongation at break, and both quantities tend to increase together. The explanation is not certain, but high values of both factors probably result if the leather has an appropriate amount of fibre splitting, and, if this is the main cause of the correlation, it emphasizes the importance of this particular characteristic. (6) There is only a moderate correlation between the strengths of pairs of specimens when one of a pair is taken from the shoulder and the other from the official sampling position in the same butt; in other words, the strength of a butt specimen affords little information regarding that of the shoulder range. In view of the possible implications of the last result for sampling problems it was decided that further experiments should be performed, and samples were taken from nine positions, more or less uniformly distributed over the area of each of the curried butts. These experiments showed that:- (7) Tensile results for the Official sampling position gave satisfactory correlations with the mean values for all the locations in the butts (the shoulder range being excluded). In other words, the shoulder range gives exceptional values that are not closely related to the strength of the remainder of the same hide, and, if this area is left out of account, the strength of a specimen from the Official position gives a fair guide as to the mean strength of the butt as a whole. For this purpose, specimens from the Official position are as satisfactory as those from any other location. (8) While extra information about the strengths of butts could be obtained by testing samples from two or more locations instead of those from one location only, the value of this extra information would hardly be sufficient to

warrant the extra cost and labor involved. (9) There is evidence that the variability associated with leathers from the same tannery depends to a certain extent upon the location chosen for testing. The data show that the Official sampling position is not a favorable one in this respect, but there evidence is not strong enough to warrant the recommendation of another location to replace it. (10) At the Official position the standard deviation of the tensile strength of nominally similar butts is about 600 lb. per sq. in. (11) Contour maps, showing how various properties alter with location in the bend, are given. For tensile strength, breaking load, and elongation at break there is no correspondence between the contours and the generally accepted views regarding the dependence of quality on location. For this and other reasons, it is suggested that the tensile test, although of some value for the detection of grossly inferior leather, is quite unreliable as a means of ranking a collection of normal leathers in an approximate order of merit. (12) On theoretical grounds it is suggested that a buckle tear test might be of more value than determination of tensile strength. The breaking loads in the two types of test are not unrelated to one another, but the correlation coefficient is low, and differences of tensile strength account for less than 10 per cent of the differences in tearing loads. (13) The contour map for buckle tear shows that the variation of this property over the butt is similar to that of leather quality, as generally accepted. This supports the view that the buckle tear test might be of value for comparing leathers from different tanneries, but no direct evidence on this point is available. (14) For the comparison of the buckle tear test of leathers of different thicknesses, the load at tear may be divided by the thickness. The quantity so obtained is practically independent of thickness, and so is free from bias.

Nitrocellulose Emulsions for Leather Finishes. By J. Creasy. *J. Soc. Leather Trades' Chemists*, **34,** 113 (1950). Oil in water emulsions of lacquer finishes offer several advantages over straight lacquers. For example, when the emulsion is applied to leather the water is lost by evaporation and absorption, leaving a smooth film on the leather surface. A lacquer too viscous to spray may be emulsified to give an emulsion of spraying consistency. Emulsions may be thinned with water, thus economizing on expensive solvents. Several formulations are given to illustrate the principles of emulsion technique applied to leather lacquers.

Committee on the Analysis of Vegetable Tanned Leather. Progress Report I. By G. Forsythe. *J. Soc. Leather Trades' Chemists*, **34,** 219 (1950). The Committee agreed to investigate more rapid methods of analysis for general use to make a complete review of existing methods of analysis of vegetable tanned leathers in the light of recent developments, and to examine possible modifications of the whole scheme of analysis, including sampling, so as to meet the modern requirements of the industry.

Trials with Benzene Hexachloride in the Protection of Hides and Skins Against Insect Damage. By H. M. French and R. R. LeG. Worlsey. *J. Soc. Leather Trades' Chemists*, **34,** 211 (1950). Because of the isolation of small collecting centers for East African hides, the time elapsing between assembly and shipment of the hides lays them subject to damage by the hide beetle, (*Dermestes maculatus*) and the larger beetle (*D. lardarius*). The cheapest effective insecticide is a sodium arsenite solution containing 0.15 to 0.20 per cent As_2O_3 equivalent, and is ordinarily used as a spray or dip. Because of its poisonous nature strict supervision must be exercised in its use, a condition very difficult to impose up-country. Moreover, when it is used as a dip, the hides do not dry out satisfactorily in the wet season, and in consequence they are subject to putrefactive damage. To overcome these disadvantages occurring with arsenite the authors selected the gamma isomer of benzene hexachloride which can be used in concentrations unlikely to be lethal to man.

It was found that this material effectively prevented insect damage to hides for at least 6 months when they were sprayed on flesh and hair sides with 500 ml. of solution containing 0.025 per cent of the gamma isomer. Seventy ml. were found to be sufficient for goat and sheepskins. Commercial preparations of the gamma isomer bearing the trade names MGO 45 and Toxaderm provided stable emulsions and comparable protection when the spray solution contained the specified percentage of the insecticide, and when not less than 5.56 mgm. per square foot were applied to hides (both sides) and 5.38 mgm. per square foot to skins (both sides). Unstable emulsions or suspensions did not give the same degree of protection.

Studies in Chrome Liquors. XIV. By T. C. Thorstensen and E. R. Theis. *J. Soc. Leather Trades' Chemists*, **34**, 230 (1950). Basic chromium sulfate, ferric sulfate, aluminum sulfate, and basic zirconium sulfate solutions containing 10 grams of the respective salts per liter were titrated with sodium hydroxide and the pH values determined electrometrically after each addition of alkali. Following this, masking agents in the form of sodium formate, acetate, citrate, oxalate, tartrate, and glycolate were added to some or all of the solutions and their pH values obtained on titration with alkali.

In the case of chromium, there was evidence of varying degrees of stability caused by complex formation with all of the stabilizing salts studied. With iron and aluminum, a remarkable similarity in their complexing properties was found. There were no stable complexes formed upon the addition of formate or acetate to iron or aluminum solutions. With the addition of salts of the hydroxy acids stable complex formation resulted. These data are in line with the investigations of other workers in this field. Evidence is presented for the formation of glycolato complexes with iron, aluminum and chromium through the coordination of the hydroxyl group of the glycolate with the metal atom and the release of a hydrogen ion into the solution. Evidence is given which indicates the real reason for the success of the use of sodium or calcium formate in conjunction with chrome liquors and their more or less failure with aluminum or iron solutions. The formates increase the stability of the chromium complexes to just the right degree (over those of sulfate complexes) and thus, materially aid the tanning action. Formates do not increase the stability of the aluminum or iron complexes and, therefore, do not add to their tanning reaction.

Note on the Determination of Chromium by Persulfate Oxidation. By J. Gagliardi. *J. Soc. Leather Trades' Chemists*, **34**, 219 (1950). Ammonium persulfate can be used satisfactorily for the wet oxidation of chrome liquors and chrome leather, giving slightly higher results than the perchloric acid method. It is regarded as safer than the latter, however.

The Use of Cation Exchange Resins for Determining Salts Content of Vegetable Tanning Materials. By J. D. Tolliday, G. W. H. Thompson and G. Forman. *J. Soc. Leather Trades' Chemists*, **34**, 221 (1950). The authors found that the exchange resin Zeokark 215 was the most satisfactory for their work. The method for determining the salt content of tan liquors was as follows: the resin was converted to the hydrogen form by percolating through it 100 ml. of 1.0 *N* hydrochloric acid during 15 minutes. The resin remained in contact with the residual acid over night and then back washed with distilled water until the pH of the wash water was above pH 5.0. Then 100 ml. of tannin solution of the required strength was percolated through the resin in 5 minutes followed by 100 ml. of water in 5 minutes, and finally the resin was back washed with distilled water until the total volume of percolate and wash water was 400 ml. The solution was then titrated with standard NaOH solution, using the glass electrode, to the required pH. Nitrogen was bubbled through the solution to prevent CO_2 absorption during the titration. Then 100 ml. of the

original tannin solution diluted to 400 ml. was titrated under like conditions. The salt content was calculated from the difference between the two titrations at usually pH 6.5. Several factors were found to affect the accuracy of the results. These were the pH of the endpoint, the concentration of the solution under examination, and the time of percolation. The mineral constituents of a myrobalam extract were determined, expressed as milligram equivalent in cation, and their sum compared with the cation determination by the exchange resin method. Agreement was within one per cent. Some determinations of the salt-acid contents of sound and rotten myrobalam nuts indicated that deterioration of the nuts is accompanied by the formation of acid soluble at pH 6.0, which cannot be ellagic or chebulinic. The Official method of extraction of raw tanning materials is criticized on the grounds that it does not extract salts as completely as plant procedure.

Tannages which Save Chromium. By H. Herfeld. *Gesammelte Abh. Dtsch. Lederinst*, **2**, 73 (1949). Through *J. Soc. Leather Trades' Chemists*, **34**, 314 (1950). The physical properties and chemical composition of chrome leathers prepared in the laboratory and on semi- and full industrial scales are compared after ordinary tannage and after the use of assistants (Blankorol A, Blankorol B, basic aluminium salts; Koreon P; Novaltan CA; Coriagen N, a polymeric phosphate; Lorikal; Ferrigan P, an anionic iron complex) designed to cut down the consumption of chromium and incorporated before, during, or at the end of the main tannage. Several of the assistants act as tanning agents, but their main function is to increase the uptake of chromium from the liquor so that, although weaker liquors are used in tanning, the finished leather still has a chrome content approaching the normal figure. Indeed, very limited economies can be made by reductions in the chrome content of the leather: a high-quality leather must contain at least 2.5 per cent Cr_2O_3. Decreased chrome uptake leads to hardness and loss of fullness, least marked with Blankorol B, most marked with Coriagen N and Koreon P. The chrome content of the liquor may be reduced to 1 per cent of the pelt weight (normal values 1.6—2.4 per cent), but below this, the leather becomes hard and empty and the grease uptake is excessive. The total ash (less chrome) must not exceed 2 per cent. Changes in physical properties resulting from the use of assistants are appreciable only with respect to water absorption, which is increased, especially with Koreon P and Novaltan CA, and shrinkage temperature, which is reduced (the least reduction occurring with Blankorol B and Coriagen N). Ferrigan P is used to replace the chrome completely; the leather requires a higher degree of tannage than a normal chrome tannage. It is correspondingly fuller but less soft and flexible, and has properties more closely resembling a vegetable tanned leather. Water absorption is much higher than in chrome leather.

Observations on the Protein Constituents of Animal Skin. By N. V. Chernov and V. E. Kotina. *Legkaya Prom.*, No. 8, 22 (1949). Through *J. Soc. Leather Trades' Chemists*, **34**, 315 (1950). The interfibrillary proteins of the skin are generally separated into the water-soluble albumins, the brine soluble globulins, and a third fraction, soluble in alkali, and regarded by some workers as a mixture of mucoproteins and by others as degradation products of epidermal and cellular tissues. Studies were made of the existing methods for extracting proteins, and errors deriving from them are discussed. Pavlov has recommended preliminary treatment of tissues with alcohol and ether before the fractionation of the protein. The authors showed that an extract of calfskin in 95 per cent alcohol, when filtered, evaporated and dissolved in water, gave a positive reaction for arginine. Extracts of protein obtained by treating skin in turn with water, salt and alkali solutions were found to contain the same protein constituent, which gave a positive tryptophane reaction even after repeated extraction with the same solvent, and it seemed unwise to fractionate protein by means of these solvents. Instead, the soluble protein could be precipitated in

three different ways: by boiling at acid pH (to remove albumins and globulins), by copper hydroxide (precipitating undegraded proteins and gelatin), and by tannins (precipitating all proteins and almost all their decomposition products). It was also shown that the fraction of total nitrogen removed from skins by alkali was the same as that removed by separate extraction with salt and alkali, or by water, salt and alkali. Extraction of the reticular layer of the skin with salt solution, however, yielded a residue which did not give a tryptophane–positive extract when treated with alkali. Other workers who have claimed the existence of a separate alkali soluble fraction in the reticular layer are thought to have relied upon too few extractions with the initial salt solution. The present experiments showed that, for complete extraction of salt soluble proteins from skins, at least 7 treatments are required; also that certain proteins of the skin dissolved more easily when salt and alkali are mixed and can exert a complex ion effect. Solutions of skin proteins boiled at acid pH lose only one-third of their total N; precipitation by copper hydroxide and tannins removes more than half. It thus appears that protein materials of a high complexity are present in solution. If a high proportion of degradation products were present in the solutions, greater differences in precipitated N would be found between the copper hydroxide and tannin fractions such as exist in putrid soak liquors. Thus, while the evidence for a mucoprotein fraction in the soluble proteins of animal skin rests insecurely on the basis of alkali-solubility alone, the further evidence given by precipitation shows that soluble proteins other than albumins and globulins are present in animal skin.

Standardizing the Bating Process. By V. G. Babakina. *Legkaya Prom.*, No. 9, 15 (1949). Through *J. Soc. Leather Trades' Chemists*, **34**, 316 (1950). The activity of pancreatic bate was found to depend upon the fineness of grinding of the raw material and the medium used for extraction. The most efficient extraction was obtained with ten times the volume of *N* salt solution at 38°C. When an aqueous or saline extract of pancreas was shaken continuously, however, some 50 per cent of the activity was lost after 15 minutes and 80–100 per cent after 3 hours. Inactivation also occurred on bubbling air, oxygen, or nitrogen rapidly through the extracts, and it is thought that shaking or similar mechanical action may bring about a separation of the prosthetic group from the main protein fraction of the enzyme. The presence of large molecules was found to protect the enzyme from mechanical impact, and extraction of the gland with 5 per cent gelatin solution gave a liquor of the same activity as a salt extract and prevented loss during shaking. Similarly, loss on shaking could be prevented or retarded by addition of protein degradation products in hide broth or spent deliming liquor. It is therefore a disadvantage in bating to use a clear aqueous extract, and efficiency will be improved in the presence of deliming liquor.

Retention of Fat Substitutes in the Currying of Vegetable-Tanned Leather. By H. Herfeld and F. Stather. *Gesammelte Abh. Dtsch. Lederinst.*, **2**, 52 (1949). Through *J. Soc. Leather Trades' Chemists*, **34**, 317 (1950). Investigations have shown that the fat substitutes developed for use on vegetable-tanned leather are only partially deposited within the fiber structure, where certain of them undergo strongly marked changes (decreased extractability and iodine value, and increased acid number) without any definite evidence of chemical combination with the collagen or leather. With some products, on the other hand, three is positive evidence of chemical combination, greatest with untanned collagen and becoming less with increasing tannage but still noticeable in full-tanned hide powder. This combination to some extent runs parallel with a marked decrease in iodine value. Nevertheless, a marked decrease in iodine value of the fat substitute after currying does not necessarily mean that combination with the fat preparation has occurred. With three substitutes, the combination of the fat and the hide is due to the fatty acid component of the substitute material.

Mechanization Problems in the Leather Industry. By. I. K. Kvyatkevich and L. P. Shuster. *Legkaya Prom.*, No. 6, 8 (1949). Through *J. Soc. Leather Trades' Chemists*, **34,** 317 (1950). At a recent conference on the subject of mechanization of the leather industry, the following recommendations were made: 1. Replacement of hand operations by machines wherever possible, e. g., in scudding, dyeing and finishing (by use of brushing machines), and currying. 2. Improvement of existing plant in order to improve leather quality and increase productivity. Measures discussed included changes in drum pegs to decrease tearing, changes in rotary buffing machines, improvements in the suspension of drums, use of paddles, separate machine drives, adjustments to friction drives and other parts, especially on unhairing and fleshing machines, combining the operations of fleshing and unhairing in a single machine, improvements in pulverizing machine draught fans, increasing movement of leather through the tannery, and increasing the working speed of machinery. 3. Increasing the number of knives and the diameter of the knife roll in appropriate machines, provision of variable-speed drives, use of single pedal shaving machines, abandoning table unhairing, removal of water by rolling machinery or centrifuge, improvements in existing types of glazing, pressing, buffing machines. 4. Development and trial of new methods by pilot plant.

Longitudinal Tensions Set Up in Leather on Glazing. By A. A. Frindlyand. *Legkaya Prom.*, No. 8, 28 (1949). Through *J. Soc. Leather Trades' Chemists*, **34,** 319 (1950). The forces acting upon leather during glazing are considered. Coefficients of friction on surfaces of different cylinders range between 0.24–0.49 for calf leathers and 0.26–0.55 for goat. They are progressivley reduced with glazing cylinders of glass, agate, jasper, and steel. Coefficients of friction of the flesh of chrome calf and goat on the surface of different belts covering the glazing table vary from 0.69–1.42. When leather is correctly tanned and the glazing machine is correctly adjusted, there is no pull during glazing; but when the coefficient of friction of the flesh to the belt is less than that of the roller to the grain, the leather is pulled from the hand of the operator. To find the effect of varying the pressure of the glazing cylinder, leathers were examined after the application of heavy and light cylinder pressures. High pressures always caused weakening of the leather (measured by tensile strength, tension at grain crack, and bursting strength) and increased its stretch. These changes were not due to the increased temperature, since samples pressed with an iron at 100°C. suffered no appreciable change. Moreover, since chrome leathers are resistant to high pressures, the effect of pressure alone is unlikely to explain the differences found, and loss of strength is probably due to the longitudinal tensions set up in the leather by friction. Similar forces will arise during other mechanical operations. Careful attention to the glazing process is therefore essential if the leather is not to be weakened, and detailed study of the longitudinal tensions induced by mechanical operations is an important future line of research.

Effects of Rolling on the Properties of Leather. By A.A. Frindlyand. *Legkaya Prom.*, No. 5, 11 (1949). Through *J. Soc. Leather Trades' Chemists.* **34,** 320 (1950). A review of Russian work since 1927 on the effect of rolling leather on its physical properties and fiber structure.

Action of Proteolytic Enzymes on Collagen. By R. E. Neuman and A. A. Tytell. *Proc. Soc. Exptl. Biol. Med.*, **73,** 409 (1950). Through *Chem. Abstracts, A. C. S.*, **44**, 6451 (1950.) Collagens from a variety of scources, prepared by methods designed not to alter properties, were resistant to the action of trypsin, chymotrypsin and papain, but were readily attacked (solubilized) by the proteolytic enzymes(s) of *Clostridium histolyticum* culture filtrate and by pepsin. *Cl. perfringens* (*welchii*) filtrate was 0.1—0.05 as active as

Cl. histolyticum filtrate in degrading collagen. The reported increased solubilization of collagens in water at the shrinkage temperature (68-70°C.) after incubation with trypsin and washing is attributed to residual (adsorbed) enzyme. Denaturation of collagen by heat or urea solution makes it susceptible to the action of trypsin and other common proteolytic enzymes. The use of hide powder as substrate in testing for collagenase activity is not valid.

Quinone Tanning in the Animal Kingdom. By H. Burton and J. L. Stoves. *Nature*, **165**, 569 (1950). Through *Chem. Abstracts*, *A. C. S.*, **44**, 6452 (1950). Dilute aqueous solutions of 2, 4, 5-trihydroxytoluene and of hydroxyquinol, applied to human skin, lead to brownish black staining. The authors suggest that these compounds function as reducers of -S-S-linkages of keratin and that the reaction products (-SH and hydroxyquinone) react further to give a thio compound which might undergo oxidation to a thioquinone. The end result is incorporation of the quinone in the protein chain. In combination with Fe this could lead to black pigment formation. Dyeing experiments on wool tend to support the hypothesis.

Determination of Total Iron in Water. By G. Gad and M. Manthey. *Gesundh.-Ing.*, **71**, 27 (1950). Through *Chem. Abstracts*, *A. C. S.*, **44**, 6552 (1950). Methods for the determination of total iron with KCNS were reviewed and a rapid method using KCNS, HNO_3 and $KMnO_4$ is described. Dilute 50 ml. of a 25 per cent solution of pure HNO_3 with 150 ml. distilled water, boil, and after cooling add 4 ml. of saturated $KMnO_4$ solution. Shake 10 ml. of this solution with 100 ml. of the water to be tested and after 5 minutes add 5 cc. 10 per cent KCNS solution. Compare the red color with standard. If manganese is to be determined in the same sample as total iron, the following procedure is proposed: Boil 100 ml. of sample with 6 ml. HNO_3 for 2-3 minutes, add a slight excess of $AgNO_3$ to precipitate chlorides and 0.5 g. $K_2S_2O_8$. Boil until the liquid becomes clear. Compare the $HMnO_4$ color with standard.

The Linkage of the Amino Group in Heparin. By J. E. Jorpes, H. Boström, and V. Mutt. *J. Biol. Chem.*, **183**, 607 (1950). Through *Chem. Abstracts*, *A. C. S.*, **44**, 6455 (1950). Heparin contains only a trace of acetic acid, probably due to impurities. The amino group of glucosamine in heparin is not linked to any aldehyde. When heparin is boiled in *N* NaOH, it depolymerizes and loses 75 per cent of its anticoagulant activity in 5 minutes. Very little amino N appears even after 1 hour. If this heparin is subsequently hydrolyzed with 0.04 *N* HCl, free H_2SO_4 appears at the same time and rate as the amino groups.

Mechanism of Action of Amino Acid Decarboxylase. II. By N. Bargoni. *Ricerche e studi med. sper.*, **17**, 313 (1946). Through *Chem. Abstracts*, *A. C. S.*, **44**, 6459 (1950). 3,4-Dihydroxyphenylalanine (0.004 *M*) was decarboxylated with kidney or liver extracts (1.5 cc.) in the presence of dithioglycolic acid (0.01 *M*), *m*-dinitrobenzene (0.003 *M*), alloxan (0.03 *M*), and isatin. These latter substances could not be proved to act as H acceptors, so that the theory of Knoop [*Chem. Abstracts*, *A. C. S.*, **30**, 25 (1936)] cannot be confirmed experimentally.

The Enzymic Synthesis of Peptide Compounds. By E. Waldschmidt-Leitz and K. Kühn. *Z. Physiol. Chem.*, **285**, 23 (1950). Through *Chem. Abstracts*, *A. C. S.*, **44**, 6459 (1950). The synthesis of amides from hippuric acid and various amines by means of papain was studied. In a typical experiment 15 cc. of a solution containing hippuric acid and aniline in a molecular ratio of 1:2 (3.23 g. hippuric acid, 3.54 g. aniline, 55 cc. 0.1 *M* citrate buffer of pH 5.0 diluted to 100 cc. with water), 5.20 cc. of a papain solution (112.5 mg. papain

Merck containing 70 papain units, dissolved in 12.5 cc. 0.005*M* citrate buffer at pH 5.0 and filtered), and 0.72, 2.16, or 5.20 cc., respectively, of a cysteine solution (0.540 g. cysteine hydrochloride-H_2O neutralized to pH 7.0 with NaOH and diluted with water to 18.0 cc.). The samples of this mixture were kept for varying times in an air-tight atmosphere of O-free N. Decrease in acidity was determined by titration with 0.2 *N* NaOH. The percentage of synthesis after 30 days, and m.p. of the compounds (uncor.) are given below: *o*-toluidine 20, 198-200°C., *m*-toluidine 67 (10 days) 186°C., *p*-toluidine 56 (10 days) 207-8°C., *o*-aminophenol 46, 199°C., *p*-aminophenol 48, 232°C., *o*-anisidine 13, 119-20°C., *p*-phenetidine 90, 203°C., *p*-aminobenzoic acid 28, 274°C., sulfanilic acid amide 12, 246-7°C., *o*-phenylenediamine 54, 217-19°C., *m*-phenylenediamine 48, 260-2°C., *p*-phenylenediamine 51, 326°C. There was no synthesis in the case of the following compounds *N*-methylaniline, *o*-aminobenzoic acid, sulfanilic acid, α-aminopyridine, adenine, benzylamine, cyclohexylamine, and ammonia.

The Nature of Some Ion-Protein Complexes. By I. M. Klotz. *Cold Spring Harbor Symposia Quant., Biol.*, **14,** 97 (1949). Through *Chem. Abstracts, A. C. S.*, **44,** 6460 (1950). The problem of ion-protein interactions is considered in the light of the following questions: Number of ions held by a given protein molecule under specified environmental conditions; maximum number of sites on a protein molecule available to a given ion; strength of the bond between the protein and any given type of ion, that is, the energy of combination; influence of environment on the extent or the energy of combination; structural features in an ion which favor combination with the protein; molecular and configurational nature of the site on the protein at which a given ion is bound.

Monolayers of Collagen. By S. C. Ellis and K. G. A. Pankhurst. *Nature*, **163,** 600 (1949). Through *British Abstracts*, B11, 425 (1950). Stable monolayers of collagen can be formed on aqueous 30 per cent $(NH_4)_2SO_4$ solution (pH 4) by spreading from HCO_2H solution. The surface pressure (π) and surface potential ($\triangle V$) have been studied over the pressure range 0.01—30 dynes per cm. As the film is compressed to an area (A) <5 sq. m. per mg. the film becomes homogeneous, and $\triangle V.A$ is constant. Further compression reveals two critical areas: A_1 (1.8 sq. m. per mg.), below which $\triangle V \times A$ decreases, indicating a change in orientation, accompanied by a decrease in compressibility; A_2 (1.3 sq. m. per mg.), derived by extrapolating the linear portion of the π-A curve (1.0—0.2 sq. m. per mg.) to zero pressure. A_1 and A_2 probably correspond, respectively, to close-packing of the polypeptides with their side-chains parallel and perpendicular to the H_2O surface. Collagen spread on aqueous solutions of HCl or NaCl yields stable and reproducible films only for areas> A_1; the dependence of the two-dimensional osmotic pressure on pH and salt is then in accord with the three-dimensional Donnan theory and the Gouy-Chapman treatment of the ionic distribution in the electrical double layer. At areas <A_2, the action of both acid and salt appears to be that of "salting-out" agents, the increasing ionic strength necessitating more work to cause displacement.

The Behavior of Exchange Fats in Fatliquoring Chrome Leather. By H. Herfeld and R. Lauffmann. *Osterreichische Leder-Zeitung*, **5,** 113 (1950). Eleven exchange fat preparations, official during the war, were compared with two sulfonated train oils (Leather aviroles). Hide powder was used since Stather and Laufmann (Collegium 1933 p. 394) found that the same results were obtained with hide powder as with intact hide. The standard procedure was to soak 5 grams of hide powder in 50 ml. of water, shake 1 hour with 50 ml. of 1/3 basic chrome alum solution (1.5 per cent Cr_2O_3) then treat with the fatliquor. As fat concentration was increased the absorption of aviorole increased and that of the exchange fats also increased to variable degrees. Bound fat increased only for products

with a Mersol base. Some exchange fats gave much higher and others much lower values for bound fat than the aviroles. Increasing chrome content had little influence on fat uptake but increased bound fat from either avirole or exchange fat. Uptake by untanned hide was small. Increasing the basicity of the chrome liquor increased bound fat but had no definite effect on take-up. Strong neutralization decreased fat absorption but increased the bound fat. For aviroles, diluting the fatliquor caused an increase then a decrease in absorbed fat but a decrease in bound fat. The effect with exchange fats was variable. Increasing the pH value of avirole liquors increased both absorbed and bound fat. Bound fat (avirole) increased as time of storage was increased to 30 days and temperature to 60°C. The various exchange fats reacted in different ways to pH and storage conditions. I.D.C.

Technical Leather Questions as a Common Problem of the Leather and Chemical Industries. By Dr. Mauthe. *Das Leder*, **1**, 33 (1950). A lecture discussing tanning operations where new chemicals may be of value. As examples; wetting agents may reduce hide loss in the soaks, new masking agents for chrome liquors may be found. Some syntans prevent loss of vegetable tannin in mixtures during tanning, and this reduced loss may offset the higher cost of the syntan. When chestnut extract was not available during the war, England made firm sole leather by using warm quebracho liquors and carefully controlled addition of acid; while in Germany the same result was obtained with syntans. With syntans, corrosion problems are greater. Analytical tannin values are useful but they can not be compared if the products are greatly different chemically, as for example vegetable tannins and syntans. I.D.C.

Tanning Oils: Fish Oil and Immergan. By E. Immendörfer. *Das Leder*, **1**, 39 (1950). Historical observations on development of Immergan. An attempt was being made to chemically modify skin without depositing much tannin, so that it would lose its hydrophilic character, would not decompose or dry out horny. The active groups in the skin are the carboxyl and amino groups. The carboxyl group is not easy to esterify; for example, alcoholic hydrochloric acid will completely destroy alcohol dehydrated skin. Acylation of the amino groups with aromatic acid chlorides such as benzoyl chloride, by the Schotten-Baumann method gave a partial tannage. A paraffin mixture having an average of about 15 carbon atoms per molecule, when treated with sulfonyl chloride, yielded "mepasinsulfochloride", later named Immergan. This made a white, tough, but rather flat leather. Preliminary tanning tests are described. Addition of a little formaldehyde aided penetration of the Immegan and improved the leather somewhat. I.D.C.

New Native and Foreign Tannery Machines. By A. Brill. *Das Leder*, **1**, 86 (1950). Brief description of machines for fleshing, staking, buffing, etc.; mainly of American make. I. D. C.

PATENTS

Process for the Production of Artificial Bristles and the Like from Proteins. U. S. Pat. 2,521,738. T. L. McMeekin, T. S. Reid, R. C. Warner and R. W. Jackson, Philadelphia, Pa., assignors to the United States of America. Apl. June 15, 1944. A process of making a fiber having a tensile strength of at least about 0.8 gram per denier, comprising: kneading a mixture essentially consisting of water and isoelectric casein at about 80–100°C. until a homogenous plastic mass is obtained; forming a filament by extruding the said mass at 95–110°C. into air; stretching the so extruded chemically unmodified filament; subjecting the stretched fiber to treatment with an anti-sticking agent; then subjecting the

filament to a hardening bath; stretching the hardened filament to a length at least 50 per cent greater than its original length; and while in stretched condition again subjecting the filament to the action of a hardening bath; and drying the filament while under tension.

Production of Gelatin Solutions of Increased Viscosity. U. S. Pat. 2,522,042. F. J. Kaszuba, Binghamton, N. Y., assignor to General Aniline and Film Corp., N. Y. Apl. Oct. 5, 1948. A composition of matter, having a viscosity greater than that of an aqueous gelatin dispersion, consisting of an aqueous dispersion of gelatin containing from 0.25 to 5 per cent of the dry weight of gelatin of a copolymer of maleic anhydride with a member selected from the class consisting of vinyl acetate and esters of acrylic and methacrylic acid, said copolymer being semi-amidated with an organic amine.

Antifoamers for Proteinaceous Solutions. U. S. Pat. 2,524,309. B. B. Coyne, Seattle, Wash., assignor to American Marietta Co., Seattle, Wash. Apl. Nov. 12, 1947. A composition for abating foam in proteinaceous dispersions and suspensions of adhesives consisting of a dispersed mixture of an alkaline earth, stearate pine oil and a petroleum distillate having a boiling point between that of gasoline and SAE No. 30 lubricating oil; in which mixture the stearate constitutes from about 1 to 12 per cent by weight of the mixture, and the remainder of said mixture comprises pine oil and petroleum distillate in the ratio of at 1:1 to 7:1.

Treatment of Wool and Other Animal Fibers. U. S. Pat. 2,519,842. L. Maaskant, Arnhem, Netherlands, assignor to American Enka Corp., Enka, N. C. Apl. Feb. 18, 1948. A process of improving the physical and chemical properties of keratinaceous animal fibers , which comprises the steps of treating the fibers with a weakly acidic solution containing precondensation products of (*a*) formaldehyde and (*b*) a compound of the class consisting of resorcinol and chloro-substituted resorcinols in the preparation of which at least six mols of (*a*) per mol of (*b*) are employed, centrifuging the thus treated fibers and drying the same by heating.

Gelatin Dessert. U. S. Pat. 2,519,961. D. P. Grettie, Chicago, Ill., assignor to Swift & Co., Chicago, Ill. Apl. Feb. 3, 1949. In a process of manufacturing a gelatin product having an improved rate of gelation in an acidic medium, the improvement which comprises: adding to a gel-forming material comprising gelatin extracted from a cured gelatin-containing material a water-soluble sulfate ion-producing composition in an amount between about 1 to 10 per cent based on the dry weight of the gelatin; the said sulfate ion substantially increasing the rate of gelation of a solution of the said gelatin in the presence of the acid.

Art of Scudding Hides. U. S. Pat. 2,520,599. F. W. Henning, Cincinnati, O., assignor to American Oak Leather Co., Cincinnati, O. Apl. Feb. 4, 1948. A leather scudding machine comprising a substantially cylindrical drum rotatable on a substantially horizontal axis, said drum having a main opening in the cylindrical wall of the drum with a closure therefor, and scudding knives arranged in spaced position around the inner surface of the cylindrical wall of the drum, and scudding knives also arranged extending from the axes of the heads along the inner surfaces of the heads of the drum in radially spaced position to the outer circumferences of said heads.

Reacting a Chrome-Tanned Hide First with a Sulfonic Acid Syntan and Then with Methylol- Melamine. U. S. Pat. 2,522,666. W. O. Dawson, Stamford, Conn., assignor to American Cyanamid Co., New York, N. Y. Apl. Nov. 19, 1946. A method of

obtaining a light-resistant white chrome tanned leather which comprises reacting fully tanned chrome tanned blue stock with about 1–5 per cent of its weight of an aromatic sulfonate tanning agent and subsequently reacting the aromatic sulfonate treated stock with about 2–5 per cent of its weight of a water-soluble methylol melamine.

Tanning with Esters of Chloroformic Acid in Nonaqueous Medium. U. S. Pat. 2,523,324. R. C. Putnam, Marblehead, Mass., assignor to United Shoe Machinery Corp., Flemington, N. J. Apl. April 23, 1947. The method of tanning stock having a moisture content of from 10 per cent to 15 per cent which comprises contacting the stock with an organic solvent solution of an ester of chloroformic acid in an organic solvent, concentration of the solution being from about 10 per cent to about 50 per cent of the ester of chloroformic acid based upon the volume of the solution.

Tanning In Nonaqueous Medium. U. S. Pat. 2,523,325. R. C. Putnam, Marblehead, Mass., assignor to United Shoe Machinery Corp., Flemington, N. J. Apl. July 10, 1947. A method of tanning hide which comprises drying the hide by the solvent action of an organic liquid to bring the moisture content to from 10 per cent to 15 per cent and contacting the dried hide with an organic solvent solution containing from 10 per cent to 50 per cent by volume based on the volume of the solution of a member of the group consisting of acid chlorides of fatty acids having from 3 to 18 carbon atoms, di-acid chlorides of dibasic acids having from 4 to 10 carbon atoms, phenoxy acetyl chloride, *m*-sulfobenzoyl dichloride, trichloracetyl chloride, and chloracetyl chloride, the solvent being selected from the group consisting of the formal of the monomethyl ether of diethylene glycol and the formal of the monomethyl ether of ethylene glycol.

Tanning With Organic Isocyanates In Nonaqueous Medium. U. S. Pat. 2,523,326. R. C. Putnam, Marblehead, Mass., assignor to United Shoe Machinery Corp., Flemington, N. J. Apl. Aug. 14, 1947. The method of tanning dried hides having a moisture content of from 10 per cent to 15 per cent which comprises contacting the skins or hides with an organic solvent solution from 10 per cent to 65 per cent by volume based on the volume of the solution of at least one member of the group consisting of isocyanates of aliphatic hydrocarbons having from 6 to 18 carbon atoms, chloromethyl isocyanate, hexamethylene di-isocyanate and 2,4-tolylene di-isocyanate.

Dehairing of Hides. U. S. Pat. 2,523,486. R. A. Whitmore, Beverly, Mass., assignor to United Shoe Machinery Corp., Flemington, N. J. Apl. April 5, 1946. The method of dehairing a wet untanned hide having an electrolytic content approximately that of a fresh hide which comprises the application of an electrolytic solution having a pH value above approximately seven to the hair side only of such a hide, spreading out and pressing the hide between two electrodes, and passing an electric current through the thickness dimension of the hide while one of said electrodes is free of said electrolytic solution.

Leather Skiving Machine or Splitter. U. S. Pat. 2,524,013. R. W. Hall, Cincinnati, O., assignor to The Randall Co., Cincinnati, O. Apl. July 19, 1947. In a material splitting machine, the combination of a bed, a head superposed upon the bed, a feed table attached to the head, a carriage slideable upon the head toward and from the bed, a lower feed roll journaled for rotation and supported upon the head, an upper feed roll on the carriage, a continuously moving band knife having a section running in substantial parallelism with one of the feed rolls, motion transmission means for elevating and lowering the carriage to vary the spacing of the feed rolls relatively, a vertically bored extension on the carriage overlying the feed table, a vertical pressure pin slidable in the bore of said extension and

having an end extending downwardly therefrom into contact with the feed table, yielding means urging the end of the pressure pin against the feed table to urge the carriage and the upper feed roll toward an elevated position to overcome backlash in the motion transmission means, and a stop upon the pin to limit retractile movement of the pin in opposition to the force of the yielding means to preclude contact of the upper feed roll with the lower feed roll and with the band knife.

Leather Skiving Machine or Splitter. U. S. Pat. 2,524,014. R. W. Hall, Cincinnati, O., assignor to The Randall Co., Cincinnati, O. Apl. July 19, 1947. In a band knife splitting machine, the combination of a support, a head moveable crosswise and radially upon said support, means for controlling crosswise movement of said head, and means for controlling radial movement of said head.

Leather Skiving Machine or Splitter. U. S. Pat. 2,524,015. R. W. Hall, Cincinnati, O., assignor to The Randall Co., Cincinnati, O. Apl. July 19, 1947. In a machine of the class described, a bed, a pair of coplanar knife supporting drums vertically mounted upon said bed, means for rotating said drums, an endless band knife spanning both drums for frictional rotation therewith, one of said drums being mounted in fixed relation to said bed, a base plate mounting the other of said drums for sliding movement toward and from said one drum, means in association with said base plate for tensioning and untensioning the knife blade, said means comprising a bored sleeve support fixed to the under surface of the base plate, a bored sleeve bearing fixed to the under surface of the bed, said support and bearing being in axial alignment, inner and outer telescoping sleeves, one end of the inner telescoping sleeve being received in the bore of the sleeve support and rigidly fixed thereto, the outer telescoping sleeve being slidable within the bore of the sleeve bearing, a rotatable shaft slidable within the inner telescoping sleeve, said shaft having one end rotatably mounted against longitudinal movement in a wall of the bed, and having its opposite end threaded and extending beyond the outer telescoping sleeve, a nut in engagement with said threaded shaft end, said nut being fixed to an end of the outer telescoping sleeve in axial alignment therewith, and a compression spring in encircling relation with the inner telescoping sleeve interposed between the sleeve support and the outer telescoping sleeve, and means in association with the tensioning means indicating a proper working tension of the knife blade.

Leather Skiving Machine or Splitter. U. S. Pat. 2,524,016. R. W. Hall, Cincinnati, O., assignor to The Randall Co., Cincinnati, O. Apl. July 19, 1947. In a band knife splitting machine, a longitudinal bed, a head supported upon said bed for bodily movement relative thereto, an elongated plate translatably supported upon said bed including means to guide the head in its movements relative to the bed, a pair of coplanar rotatable drums vertically disposed at the outer ends of the bed, means for rotating said drums, a band knife tracked upon the periphery of the drums and having thereon a beveled cutting edge, a pair of motor driven grinding wheels depending from said elongated plate and translatable therewith, said grinding wheels being disposed to act upon opposed faces of the knife edge in sharpening relation therewith, means for adjusting the distance between centers of said grinding wheels for varying the length of bevel ground on the knife, means for moving said elongated plate to bring its depending grinding wheels toward and away from the band knife, said movement of the elongated plate being independent of the head movements, and means for indicating the degree of bevel being ground upon the cutting edge of the band knife.

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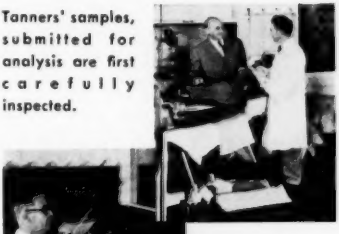
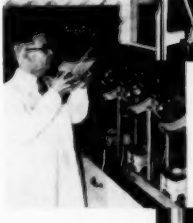


Tanners' samples, submitted for analysis are first carefully inspected.



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Na_2S	61.00

Manufactured in large tonnages by

BARIUM REDUCTION CORPORATION

SOUTH CHARLESTON 3, WEST VIRGINIA

need we say more?

a dye to remember

*Calcocid** GREEN G CONC.

When Greens are the mode, think of Calcocid Green G Conc. You will be highly pleased with the results.

Calcocid Green G Conc. is well suited for use with all types of tannages, particularly for dyeing pastels with synthetic tanning materials. It penetrates well, gives good uniform coverage, exhausts well, and glazes true.

Calcocid Green G Conc. is recommended to produce shoe upper leathers, both grain and suede, as well as bag and garment leathers.

Your Calco representative is a trained and experienced leather colorist. He will be happy to demonstrate, in your own plant, the superior working properties of this and other dyes in the complete Calco line . . . to your profit.

*Trade-mark

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CALCO CHEMICAL DIVISION.
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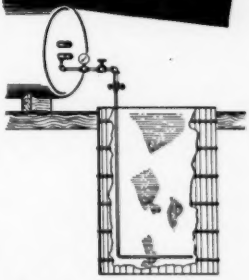

Here is a typical installation for reducing an experimental plant-size batch of chrome tanning liquor.

Write for your Ansul Bulletin No. 950.1.

LIQUID Sulfur Dioxide ANSUL*

*REG. U. S. PAT. OFF.

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